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Preservation of plywood against biological attack with low environmental impact using tannin-boron preservative

By

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Protection à faible impact environnemental des contreplaqués avec des associations tannins-bore

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Abstract

An experimental investigation was conducted to preserve plywood panels made of perishable wood species (beech and poplar) against biological attacks with low environmental impact. A newly developed tannin-boron preservative was proposed to reduce the leaching of borates. This system was used to preserve plywood with two approaches: (1) in the glue line to replace formaldehyde based adhesives and gluing wood veneers (for interior applications), (2) pretreatment of wood veneers with the diluted formulations and bonded with melamine-urea-formaldehyde resin (for humid applications). The research data in this thesis were obtained from three main groups of experiments: chemicals and thermomechanical testing on the tannin-boron resin, measuring physical and mechanical properties, and different biological tests before and after leaching processes. The chemicals testing on the tannin/hexamine adhesive showed that the addition of Boric Acid (BA) can contribute to more inter-flavonoid linkages (than when there is no BA in the glue). Also the addition of BA can open pyran rings which lead to the acceleration of polymerization reactions. Thermomechanical analysis on the adhesives of mimosa and quebracho tannins confirmed that the addition of BA lowered time and temperature of hardening, and also increased module of elasticity values of the adhesive. The addition of BA up to 5% into the tannin adhesive upgraded physical properties and tensile shear strength. An excess loading of BA (10%) in the glue line caused imperfect physical features and tensile shear strength. Despite the low uptake of BA but its addition into the tannin glue provided effective resistance against fungal attack even after mild leaching test according to the EN 1250-2. The results of termites test showed that increase in the BA content of the adhesive decrease the survival rate and the weight loss but the samples underwent a severe attack (visual ration 4). No improvement against termite attack was obtained after leaching by a choice feeding test. The plywoods made of treated veneers by tannin-boron solutions showed partially lower tensile shear strength than the control plywood, but still in the range of standards requirements for the humid applications. The results of fungal test showed that with a strong polymeric network of tannin even after severe leaching test (according to EN 84); there is significant enhancement in the durability. The control plywoods made of treated veneers with BA alone solutions presented weight loss values as much as controls against fungal attack after leaching test. The results of termite tests showed the lower survival rate and the weight loss than the controls even after severe leaching test for the plywoods made from treated veneers with the tannin-boron systems. The results of choice feeding test showed that termites preferred feeding from the controls when alternative samples were treated with the tannin-boron system. In general the evidence from this study suggests that tannin-boron system can significantly slow down the leaching of boron and it revealed high potential to preserve plywood.

Keywords: plywoods, tannin, boric acid, leaching, thermomechanical analysis, physical properties, tensile shear, fungal test, termites test.

Résumé

Une étude expérimentale a été menée afin de protéger des attaques biologiques des contreplaqués faits d'essences non durables (hêtre et peuplier), et ce, avec un faible impact environnemental. Des produits de protection à base de tannins et de bore, nouvellement développés afin de réduire le lessivage du bore, ont été sélectionnés pour ce but. Ce système a été utilisé pour protéger les contreplaqués selon deux approches : (1) au niveau de la colle pour remplacer les adhésives à base de formaldéhyde (utilisation en intérieur), (2) en traitement des plis avec des formulations plus diluées, la colle étant un adhésif mélamine-urée-formaldéhyde (utilisation en milieu humide). Les données expérimentales de cette thèse peuvent être classées en trois grands groupes : essais chimiques et thermo-mécaniques des colles tannin-bore, mesure des propriétés physiques et mécaniques, de la résistance biologique avant et après vieillissement des différents panneaux. Les essais chimiques sur les colles tannin/hexamine ont montré que l'addition d'acide borique (BA) peut contribuer à plus de liaisons inter-flavonoids (par rapport au même système collant sans bore). L'addition de BA peut ouvrir les cycles pyranes et accélérer les réactions de polymérisation. Des analyses thermo-mécaniques sur les colles contenant des tannins de mimosa et de quebracho ont confirmé que l'addition de BA abaissait le temps et la température de prise, et augmentait les valeurs du module d'élasticité de la colle. L'addition de BA jusqu'à 5% dans la colle à base de tannin augmente les propriétés physiques et la résistance au cisaillement. Une charge excessive de BA (10%) dans la colle est la cause de pertes de propriétés mécaniques et physiques. Bien qu'en faible quantité, l'introduction de BA dans la colle de tannin amène une protection efficace contre l'attaque fongique, même après un lessivage selon l'EN 1250-2. Les résultats des essais termites montrent que l'augmentation de BA dans la colle abaisse le taux de survie des insectes et la perte de masse des échantillons, mais ceux-ci présentent un sévère degré d'attaque. Aucune amélioration n'a été obtenue lors d'un essai de choix après lessivage. Les contreplaqués faits de plis traités par des solutions tannin-bore ont montré des résistances au cisaillement plus faibles que les témoins, mais toujours dans les gammes requises pour des applications en atmosphère humide. Les résultats des essais fongiques ont montré qu'avec un réseau polymère de tanins, même après un lessivage sévère (selon l'EN84) ; il y avait une amélioration significative de la durabilité. Les contreplaqués faits de plis traités avec BA seul ont présenté une sensibilité à l'attaque fongique similaire à celle des témoins après un lessivage. Les résultats des essais termites ont montré un faible taux de survie des insectes et de perte de masse, comparé aux témoins, même après un lessivage sévère, pour les contreplaqués avec des plis traités par des systèmes tannin-bore. Les résultats d'un essai de choix ont montré que les termites préféraient se nourrir des témoins quand l'alternative proposée était des échantillons traités avec des systèmes tannin-bore. En général, il a été montré dans cette étude que les systèmes tannin-bore pouvaient réduire significativement les lessivages du bore et être potentiellement très efficaces pour la protection des contreplaqués.

Mots clés: contre-plaqués, tanin, acide borique, lessivage, analyse thermomécanique, les propriétés physiques, cisaillement traction, essai fongique, essai termites.

List of abbreviations in this dissertation

Abbreviation	**Description**
AC	Copper Azole
ACC	Acid Copper Chromate
ACQ	Alkaline Copper Quat
AWPA	American Wood Preservers Association
BA	Boric Acid
BAE	Boric Acid Equivalent
BX	Borax
CCA	Chromated Copper Arsenate
CCB	Copper Chrome Boron
CB	Calcium Borate
$\mathrm{D_{od}}$, $\mathrm{D_{12\%}}$	Oven Dry Density, Conditioning Density at 20±2 °C; 65±5% RH
DOT	Disodium-Octaborate-Tetrahydrate
EN	European Norms (standards)
FAO	Food and Agriculture Organization of the United Nations
FTIR	Fourier transform infrared spectroscopy
IB	Internal bonding
L	Length of plywood samples
LVL	Laminated veneer lumber
MALDI-TOF	Matrix-assisted laser desorption/ionization time-of-flight
MC, EMC	Moisture Content, Equilibrium Moisture Content
MOE	Modulus Of Elasticity
MUF	Melamine Urea Formaldehyde
OSB	Orientated strand board
PF	Phenol Formaldehyde
PMDI	Polymeric 4,4´ -diphenyl Methane Di Isocyanate
T	Thickness of plywood samples
TMA	Thermomechanical analysis
TMB	TriMethyl Borate
UF	Urea Formaldehyde
W	Width of plywood samples
WBC	Wood-Based Composites
WPC	Wood plastic composites
ZB	Zinc Borate

List of papers in the period of application of Ph.D.

Peer-reviewed paper

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Posters

1. Efhamisisi, D., Thevenon, M. F., Pizzi, A., Hamzeh, Y., Karimi, A. N., Pourtahmasi, K. 2014. Induced hardening of quebracho tannin adhesive by boric acid to make poplar plywood. Poster presented at 22ème journée conférence de l'école doctorale (I2S) de l'Université Montpellier 2 (Doctiss), Montpellier-France.
2. Efhamisisi, D., Thevenon, M. F., Pizzi, A., Hamzeh, Y., Karimi, A. N., Pourtahmasi, K. 2014. The effects of boric acid addition on hardening rate of quebracho tannin adhesive and biological resistance of poplar plywood. Poster presented at Journées scientifiques, GDR Sciences du Bois, Nancy-France.

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CHAPTER 1: Introduction to the present study

1.1 Wood and its importance

Wood is great natural resource which is used by humankind as fuel or building materials for thousands of years. It is a renewable source which can probably satisfy human need for ever.

Today, there is a general afraid in the public opinion about the impact of greenhouse gases on the global warming. The forestation and the use of wood as raw material for construction and even as fuel can play an important part in reducing greenhouse gases emissions. Wood construction and the use of wood products have two key positive environmental and climatic effects. Firstly, wood-based products serve as carbon stores (a cubic metre of wood contains approximately 200 kg of carbon, which equals approximately 750 kg of carbon dioxide). Secondly, wood can often be used in place of materials like steel, aluminum, concrete or plastics that require large amounts of energy to produce. The carbon often remains stored in the wood products for decades, or longer (Sathre & Gustavsson, 2009). It is released only when wood or wood composites burns or decomposes. On the other hand, the volatility of oil prices and the concerns about long-term supply of crude oil is caused an increasing interest to the wood fuel again ("Wood The Fuel of the Future", 2013). According to statistics released by FAO (2013) slightly more than half (52%) of the harvested roundwood is used as woodfuel. If wood used in a power station comes from properly managed forests, then the carbon that billows out of the chimney can be offset by the carbon that is captured and stored in newly planted trees. On average a typical tree absorbs, through photosynthesis, the equivalent of 1 tonne of carbon dioxide for every cubic metre's growth, while producing the equivalent of 0.7 tonne of oxygen (Reid et al., 2004).

In addition to the environmental benefits of using wood, wood has many mechanical- physical advantages compared to other building materials (Shi & Walker, 2006).

According to what has being said, wood can be the most suitable raw material for construction and energy supply from three major points of the view: environment, development and sustainability.

But wood has some disadvantages too. Wood is dimensionally unstable in uncontrolled environments and swells as it wets and shrinks as it dries. There is, also, large variability in properties of wood between same species and even within a tree. On the other hand, wood is organic and lignocellulosic material which is prone to be attacked with biological deterioration agents (Zabel & Morrell, 1992). Today in particular, there is reduction in harvesting wood from natural forest. And wood supply is replace with material obtained from short rotation plantation with fast growing trees such as poplar. For examples, more than two million cubic meters of poplar wood are harvested annually in Iran (Ghasemi & Modirrahmati, 2004). This is equivalent to 40 percent of total wood consumption by Iranian industry (Modaberi et al., 2014). The material obtained from plantation has high proportion of juvenile wood, small dimensions and sometimes lower natural durability compared to those achieved from natural forest (Zobel, 1984), which is due to the short harvesting time. In the meantime, making wood composites is an interesting alternative to overcome the problems of wood from plantation, different timbers can be combined to create a new material with homogenous properties. Wood-based composite products are commonly substituted for solid wood in today's building structures. They are manufactured in desirable size with more dimensional stability and homogeneous properties.

But the problems related to natural durability will continue to exist. Wood and items made from woody species that do not possess an inherent natural durability appropriate to the use class they are placed in, will fail in service due to the biological attack. In order to upgrade their durability, wood preservation (protection) treatment is required.

Solid wood products have been historically treated by a variety of methods. But wood-based composite products present complexities and opportunities not found in the solid wood preserving industry. In any case, a preservative-treated wood composite product must provide adequate protection without sacrificing mechanical or physical properties.

1.2 Strategy and objectives of the present study

Wood is one of the most important renewable bioresources used by mankind in many applications in the form of solid wood or wood-based composites. Plywood is oldest known wood composite. If the plywoods made from the perishable wood species, they are also susceptible to decay by fungi and insect attack. The most of the plywoods particularly in high risk region, either external or internal application, need to be protected from biodegradation agents in order to extend service-life (EN 335, 2013).

Today, there is a general afraid in the public opinion about the impact of old wood preservatives on the environment and human health. CCA (Chromated Copper Arsenate) formulations have been the most used formulations for the treatment of wood and plywood by post manufactured treatment. But CCA has developed a great concern from the environment and human health standpoints. As a result, in Europe and North America arsenic is prohibited from most of the applications for preserved wood.

In the meantime boron-based systems are candidates for the future range of preservative formulations with lower environmental and health impacts. Borates such as boric acid (BA) have been used in wood preservation for over 40 years. They present many advantages to preserve the wood against biodegradation agents. They are more effective preservatives than copper and zinc (Freeman et al., 2009), but their high solubility and susceptibility to leaching is the main obstacle to the widespread use of them. Recently, several attempts have been made to stabilize the boron in the wood. In this regard Pizzi and Baecker (1996) described a mechanism in which BA was used to induce autocondensation of condensed tannins. Then the BA can partially fix to the network by the autocondensed tannin. Further work revealed that hardening of condensed tannins by hexamine in alkaline environment, when BA is complexed onto the network; markedly slow down the leaching of boron (Thevenon et al., 2010 and 2009). In this system, there is interaction between tannin and BA. First, BA induces tannin autocondensation and then BA can partially fix to the tannin network. This system gives enough mobility to boron to be active as biocide while also reducing its leachability to some extent.

In this regards, we became interested about condensed tannin properties for borates fixation. And an idea took shape to use this system for environmentally favorable protection of plywood against biodegradation.

The veneers of two woody species including poplar and European beech were selected to make plywoods. These timbers were chosen because of their low durability against biodegradation. Poplar and beech, on the other hand, are easily accessible in Iran and France .Beech is one of the major forest trees in Europe (Brunet et al., 2010), and is considered as standard species in European norms for wood science studies. Beside, poplar plantation has a very important role in cellulosic resources and reducing pressure on natural forests.

This thesis shall contribute to evaluate possibility of use tannin/boron system to protect plywood panels against decay and degradation with two approaches:

1) Glue line treatment to make plywood for dry condition

First idea is to use of more concentrated solutions of tannin/hexamine which can be used as an adhesive for making plywood. So BA can be added into this system for a number of reasons: (1) increase tannin hardening rate, (2) upgrade mechanical properties (3) fixing BA and provide biological resistance.

2) Pretreatment of wood veneer to make plywood for humid conditions

In this approach prior to gluing/pressing, wood veneers will be treated with different formulations of tannin/hexamine + BA. Then, theses veneers will be bonded together with Melamine Urea Formaldehyde (MUF) to make water resistance and durable plywood. It is expected to have acceptable durability even after leaching with this approach.

The Hypothesis

1. The addition of BA into the tannin glue can accelerate hardening reactions and upgrade mechanical properties,
2. BA can be linked to the tannin/hexamine resin and partially fixed against leaching,
3. The addition of BA into the tannin glue or treatment of veneers with tannin/boron system can improve resistance against both fungi and termites attack.

The objectives

The main objective of this dissertation is preservation of plywoods which are made from perishable woods against biodegradation agents relying on eco-friendly way. This was studied with following cases:

1. Fixing BA with autocondensed tannin in wood and reducing its leaching,
2. Making outdoor plywood with treated veneers (tannin/BA hexamine) bonded to each other's with MUF,
3. Making indoor plywood by replacing the formaldehyde adhesive by tannin/hexamine adhesive added with BA,

4. Conducting several experiments on the tannin adhesive to bring more information on the effect of BA addition on thermomechanical characteristics and polymerization of tannin adhesive,
5. Evaluation of physical-mechanical properties of all plywoods,
6. Conducting several biological tests, before and after different leaching processes, to evaluate the efficacy of tannin network in fixing BA,
7. Since there is no termite test standard, so far, for wood-based composites in Europe, using the existing standard methods of termite test (EN117 and EN118) on plywood samples will be discussed.

1.3 Outlining the structure of the presentation

My thesis is composed of different themed chapters. Following this short introduction, it will then go on to chapter 2. This chapter first gives basic definitions about the issues involved in this study. Then it continues with reviewing details and theoretical dimensions of the current research in the resent published papers. The third chapter covers the detail of materials used and the manner of making plywoods. The fourth chapter concerns the methodology used for testing chemical-physical-mechanical properties and biological features. The remaining part of this manuscript presents the findings of the research, focusing on the three key themes: results of preservatives uptake and retention as well as testing on the resin (chapter 5), physical-mechanical properties (chapter 6), and biological tests (chapter 7). General conclusions and perspectives are finally proposed in last chapter.

CHAPTER 2: Overview of current knowledge from research

2.1 Wood-based composites

As previously mentioned, wood has itself natural heterogeneity and anisotropy as well as dimensionally unstable in uncontrolled environments. On the other hand, the quality of wood supply has changed recently, that is related to the trends toward harvesting from short-rotation forestry and plantations of fast-growing trees (Zobel, 1984). It results in small-sized timber, low-quality wood, and a high proportion of juvenile wood and knots. In this regards, making composites is an interesting way to reduce impact of wood heterogeneity and a solution to deal with changes in wood supply. Nowadays, plantation plays a big role to supply the timber for industry and reduce the major wood deficit.

Recently, much progress has been achieved in the production technology of different kind of the wood-based composites (WBC). There is a broad range of WBC, but they are grouped into three general categories from the standpoint of the size and nature of the components: veneer-based material, particle and fiber composites, and wood–nonwood composites (Youngquist, 2010). Veneer-based WBCs most closely resemble to solid wood. But their physical and mechanical properties are highly better than the solid wood that they are made from. They are manufactured in desirable size with more dimensional stability and homogeneous properties (Shi & Walker, 2006). But their use is often limited due to high sensitivity to decay and degradation like wood. So, when they are used in outdoor application and even indoor conditions, proper protection is important to ensure a long service life (Laks 2002; Tascioglu et al., 2013).

2.2 Plywood

The oldest known WBC is plywood. Thousands of years ago Chinese and Egyptians shaved wood and glued it together to achieve a stiffening effect with veneered surfaces. Commercial plywood started in the seventieth and eighteenth centuries, as a result of work carried out in England and France (Shi and Walker, 2006). Plywood is a flat panel built up of sheets of veneer called plies, united under pressure by an adhesive to create a panel. It is always constructed with an odd number of layers with the grain direction of adjacent layers oriented perpendicular to one another (Youngquist, 2010). In recent years due to lack of suitable raw material, the production of plywood has been insignificant in Iran. Hence the needs of consumers are mainly supplied by imports (Figure 2.1). Furthermore, another part of needs is replaced with other type of WBCs like particleboard, medium-density fiberboard (MDF), and oriented strand board (OSB).

In France, the amount of production is not comparable to Iran. However plywood production, import, and export have decreasing trend in recent years (Figure 2.2). In fact, plywood production with log peeling method needs a minimum of log diameter. With the advent of other type of WBCs which are produced with smaller diameter wood; the production and consumption of plywood decreased to some extent.

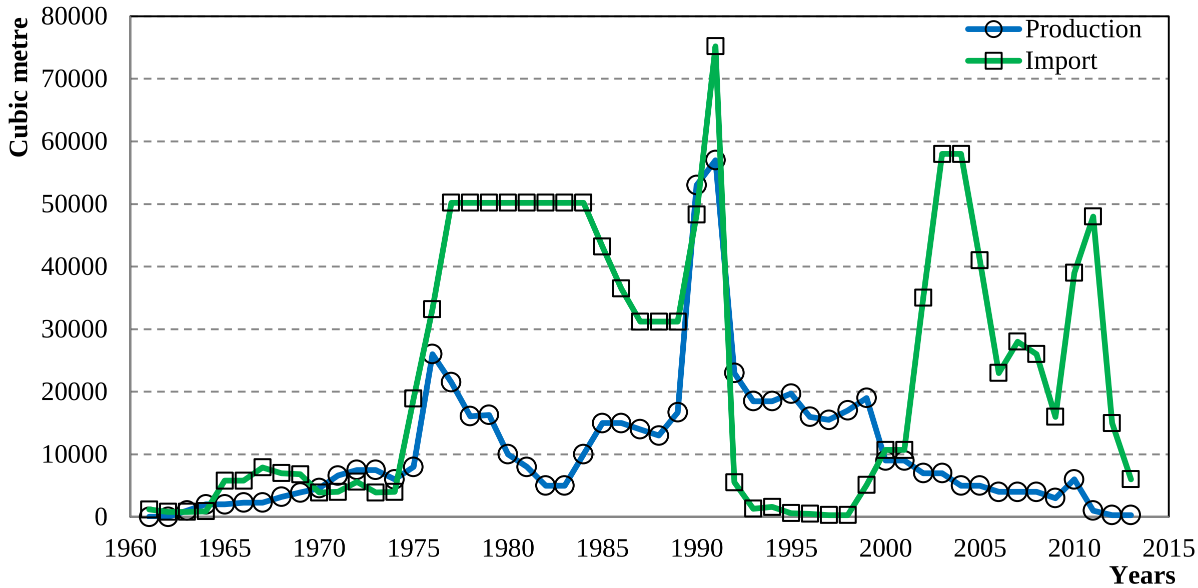


Figure 2.1 The amount of plywood production and import in Iran (FAOSTAT, 2014)

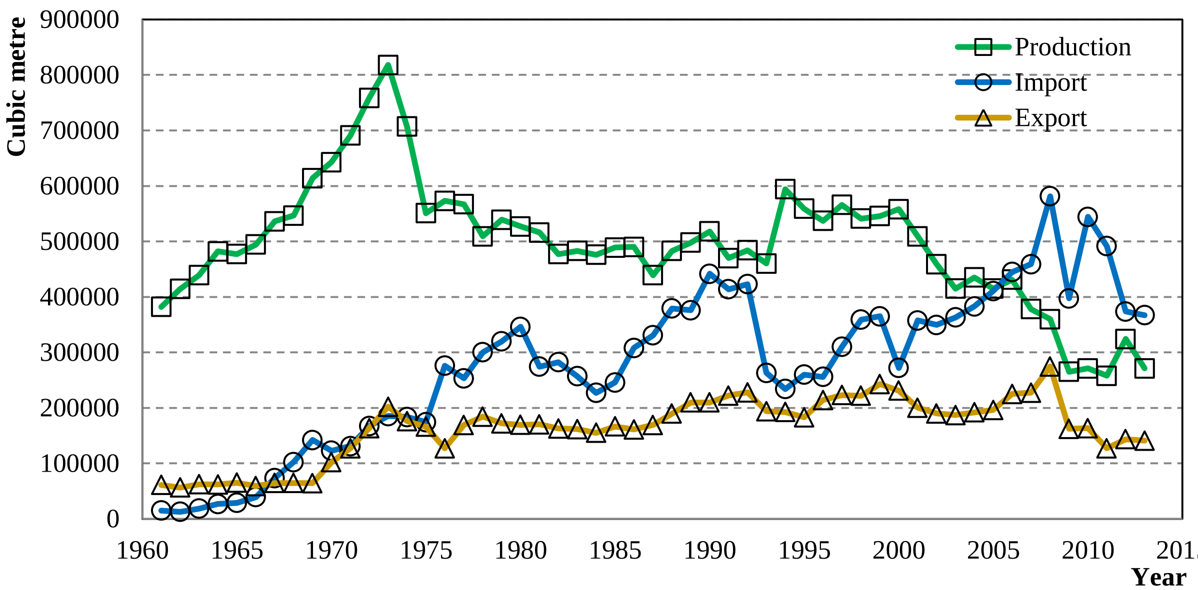


Figure 2.2 The amount of plywood production, import, and export in France (FAOSTAT, 2014)

Generally there are three kind of plywood (EN 636, 2003) based on the adhesive resistance to water exposure; and they deal with different classes of biological hazard (EN 335, 2013; EN 335-3, 1996).

2.2.1 Bond class 1 Plywood: use in dry conditions

In this environment, plywoods have a moisture content no higher than that which would result from exposure to an air temperature of 20 °C and a relative humidity of 65 % for practically the whole of their service life. They may therefore be regarded as being dry, and thus the risk of attack by surface molds or by staining or wood-destroying fungi is insignificant. Attack by wood-destroying insects, including termites, is possible but the frequency and importance of this risk depends upon the geographical region. Attack by beetles can also depend upon choice of veneer with respect to species and thickness.

2.2.2 Bond class 2 Plywood: use in humid conditions

In this environment, the moisture content of a plywood panel, either in the whole or only in part, can occasionally attain or exceed that which would result from exposure to an air temperature of 20 °C and a relative humidity of 90 %. The moisture content can therefore occasionally increase to a level which can allow the growth of wood-destroying fungi. For panels the use of which includes a decorative function, disfigurement can also occur as a result of the growth of surface molds and staining fungi. Risk of insect attack is similar to that for bond class 1.

This bond class is appropriate for protected external applications (e.g. behind cladding or under roof coverings), but is capable of resisting weather exposure for short periods (e.g. when exposed during the construction). It is also suitable for interior situations where the service moisture condition is raised above the class 1 level.

2.2.3 Bond Class 3 Plywood: use in exterior conditions

In this environment plywoods can frequently have a moisture content above 20 % and thus will often be liable to attack by wood-destroying fungi. For panels the use of which includes a decorative function, disfigurement can also occur as a result of the growth of surface molds and staining fungi. Risk of insect attack is similar to that for bond class 1. This bonding class is designed for exposure to weather over sustained periods.

2.3 Wood preservation

Wood and items made from wood are organic and lignocellulosic material which is proned to be attacked by biological deterioration agents. Wood species that do not possess inherent decay resistance properties can fail in service due to biological attack, creating a need for preservative-treated wood. For solid timber durability concerns have historically been addressed through the use of chemical treatments by a variety of application methods including pressure impregnation, immersion, diffusion, and vacuum-assisted treatments (Richardson, 2002). Wood preservatives must cover four criteria (Richardson, 2002): (1) providing the desired wood protection in the intended end use, (2) they must do so without presenting risks to people or the environment, (3) resistant to leaching, and (4) finally cost effective (Lebow 2010). Environmental performance and sensitivity of the wood preservatives are playing an increasing role in their development and use (Shmulsky & Jones, 2011).

2.4 Systems for preservation of wood composites

In many cases traditional treatment methods have not proven to be practical or effective enough for wood composites. With the exception of pressure-treated plywood, chemical treatments have not been widely used to enhance the durability of wood-based panel products (Manning, 2002).

Wood-based composite products present complexities and opportunities not found in the solid wood preserving industry. Because there are many types of wood composite products and manufacturing processes, there are a number of ways to apply preservative treatments to these materials (Gardner et. al., 2003).

There are three primary methods for manufacturing treated wood composites, based on the manufacturing process of the composite material. These methods include pretreatment of wood furnish, in-line treatment, and post treatment of finished products (Laks 1999).

2.4.1 Pretreatment of wood furnish

In this process, preservative may be incorporated into wood furnish like veneer, particle or fiber by pressurized either non-pressurized (spraying or dipping) processes with liquid-based systems (Wu 2004; Ross et. al., 2003).

2.4.2 In-line treatment

In-line treatment refers to the process whereby the active preservative ingredients are combined with dry wood furnish before mat forming and hot pressing (Lee et. al., 2004). The preservatives can be applied to wood in two ways (Wu 2004; Ross et. al., 2003; Kirkpatrick and Barnes, 2006):

- Spraying the preservative directly to dry wood furnish in blenders. This is often done for strand-based composites with powder type preservatives (like zinc borate);
- Premixing the preservative with resin and spraying the mixture to wood furnish. This process is often referred to glueline treatments and is mainly applied in products made of veneers such as LVL and plywood.

2.4.3 Post Treatment of Finished Products

Post manufacturing treatments are applied to wood-based composite products either through immersion or spray applications. These provide an envelope of protection to the substrate and are mainly designed to provide short-term resistance to mold, decay and water intrusion. Their major advantage is that they are relatively easy to apply and are very cost effective (Wu, 2004).

2.5 Wood biodegradation agents

The organisms that can degrade wood in use are principally fungi, insects, marine borers, and bacteria. Among them, fungi are the most serious threat to wood (Schmidt, 2006). Insects also may damage wood, and in many situations must be considered in protective measures. Termites are the major insect enemy of wood (FAO, 2000). They are sometimes a more serious menace than fungi. After termites, wood-boring beetles are the most important wood-destroying insects. The most common types of powder post beetles are Anobiid, Lyctid, and Bostrichid beetles (Richardson, 2002; Clausen, 2010). Other wood-infesting insects are carpenter ants and carpenter bees which have low prevalence and importance. The marine wood-borers, inhabiting the costal ecosystems, are the primary agents of wood degradation in the marine timber structures. A special type of exterior plywood is known as marine plywood which may be subject to attack by marine borers in salt water according to EN 335-3 (1996). Some applications for the marine plywoods are: boat making, lake platforms, and boat dock. Bacteria attack is an early stage in the degradation of wood exposed to the wet and moist conditions where there is no oxygen for fungal activity (Clausen, 2010; Richardson, 2002). Bacteria activity can be found on the plywoods in contact with ground or fresh water (EN 335-1, 1996). Decay fungi and subterranean termite species in Europe, pose the highest risk. The biodegradation by rotting fungi and termites are the subject of this study and more detail will be given in the following.

2.5.1 Fungi

Wood rotting fungi are able to damage any wood species and all that is needed is a source of water. The wood that has been dried and kept dry will never be rotten. Wood decay fungi cause billions of dollars in losses each year by destroying wood in forest trees or in the buildings and other wood in service (Schmidt, 2006).

Wood-decay fungi can be classified according to the type of decay that they cause. The most common types of wood decay are brown rot and white rot caused by basidiomycete fungi. Wood decay is also caused by members of the Deuteromycetes and Ascomycetes phyla, commonly termed as soft rot (Eaton & Hale, 1993).

Another type of fungi that attack to the woody material is discoloration fungi or molds. The wood-discoloring molds and staining fungi live on nutrients in the parenchyma cells of the sapwood. They do not cause any or only very little cell wall attack. These fungi mainly belong to Deuteromycetes and Ascomycetes (Eaton & Hale, 1993; Schmidt, 2006). Wood discolorations cause a cosmetic, surface damage.

2.5.1.1 Soft Rot

This type of decay was termed 'soft rot' because of the spongy texture of the wood surface in ground only situation. Soft-rot fungi decay wood under extreme ecological conditions, terrestrial and aquatic environments, which are unsuitable for Basidiomycetes. Soft rots are chemically and macroscopically more similar to brown rots than white rots since cellulose and hemicellulose is decomposed while lignin is modified slightly (Schwarze, 2007).

2.5.1.2 Brown rot and white rot

Brown rot and white are serious problem for wooden constructions in service both in ground and above ground situations (Eaton & Hale, 1993).

Brown rot is caused by Basidiomycetes, which metabolize the carbohydrates cellulose and hemicelluloses of the woody cell wall by non-enzymatic and enzymatic action and leave the lignin almost unaltered. Brown-rot fungi do not produce lignin-degrading enzymes. The residual wood is brown and often cracks into cubical pieces when dry (Schmidt, 2006). Brown rot fungi are the most prevalent cause of decay in softwoods (Milton, 1925)

White rots are mainly caused by basidiomycetes and by certain ascomycetes. The common feature of all these fungi is that they can degrade lignin as well as cellulose and hemicelluloses. However, the relative rates of decomposition of lignin and cellulose vary greatly according to the species of fungi and the conditions within the wood (Schwarze, 2007). There are two different kind of white rot: (1) preferential delignification and (2) simultaneous rot.

In preferential delignification, lignin is degraded earlier in the decay process than cellulose or hemicellulose. In simultaneous rot, the enzymes that they secrete by fungus are able to decompose simultaneously all substances of the lignified cell wall (Schmidt, 2006).

White-rot fungi occur more frequently on hardwoods (Schmidt, 2006). The decayed wood is brighter in colour with fibrous structure (Richardson 2002). White-rot fungi are grown all over the world and distribute broader over the different basidiomycetous groups (Rayner & Boddy, 1988).

Among the various species of white rotting fungi, *Trametes versicolor* has particular economic importance and it can be found all through the year and throughout the world. *T. versicolor* is the most common fungi associated with the hardwoods decay in Europe (Elisashvili, et. al., 2012), as well as in the north of Iran the most common fungi is *T. versicolor* which is used as white rotting in academic studies.

Trametes versicolor – also known as *Coriolus versicolor* – is a common fungus found throughout the world. It means 'of several colours', *versicolor* describes this fungus is found in different colors. Since it is similar to multiple colors in the tail of wild turkey; *T. versicolor* is commonly called turkey tail (Schmidt, 2006; Schwarze, 2007; Richardson, 2002) (Figure 2.3).

Figure 2.3 *Trametes versicolor* fruiting body, its cap colors are extremely variable

T.versicolor is found virtually anywhere on dead hardwoods and rarely on softwoods. It causes simultaneous white rot that is the subject of standard test of wood degradation by fungus for hardwood samples (EN 113,1996). Wood decayed by *T. versicolor* and some other fungi shows black demarcation lines, which includes mycelia that separate themselves from not yet colonized wood (Schmidt, 2006).

2.5.2 Termites

Globally, the annual economic cost of termite damage and termite prevention is estimated in billions (Ahmed and French, 2005). Termites are an essential member of the soil ecosystem and are found throughout the world. Termites are social insects living in colonies made of different individuals. There are more than 2,600 recognized species of termites. However, from the standpoint of their feeding and nesting habits, they can be assigned to three distinct groups: dampwood termite, drywood, and subterranean termites (Lewis, 2008).

2.5.2.1 **Dampwood termites**

They primary attack decaying wood and are controlled by eliminating the water moisture source that led to decay. They are not major economic problems in buildings. They are largely restricted to cooler and wetter forest regions in different parts of the world.

2.5.2.2 **Drywood termites**

Drywood termites are common on most continents and can survive in very dry conditions, even in dead wood in deserts. They do not require direct contact with a source of moisture and do not make any connections to the soil. Since drywood termites form colonies within sound dead wood, they have no access to free water. This is the reason for their common name, drywood termites. Both dampwood and drywood termites nest within their food source.

2.5.2.3 **Subterranean termites**

Subterranean termites are the most destructive insect of wood, and account for 95% of global termite damage (Wagner et. al., 2008). Subterranean termites have fixed nests, with populations numbering in the millions. Thus, the rapidity and scale of their attack on new food source is much more spectacular than that of dry wood termites. For subterranean termites, on the other hand, nesting and feeding sites are well separated but linked through a system of underground tunnels. These tunnels can also travel over steel, resistant wood, or other surfaces which the termites cannot penetrate until suit food source (Kartal and Imamura, 2004).

There are three specialized termite castes in the colony of subterranean termite: reproducers, which supplement the egg production of the primary queen or begin new colonies, soldiers, which defend the other castes from attack, and workers, which collect food, repair the colony and feed other castes (Abdel and Skai, 2011; Korb and Hartfelder, 2008).

2.5.2.3.1 **Reproducers**

Reproducers in a colony come in three general categories: The royal pair (king and queen), winged alate, and supplementary (or neotenic) reproductive (Figure 2.4). The winged alates are freshly hatched reproductive adults that will either remain in the colony to become supplementary reproductive, or travel outside of the nest to settle new colonies in the surrounding area (Lewis, 2008)

All types of reproducer termites obtained from nymphs (semimature young). They resemble workers, but have wing buds. The nymphs develop into the adult termites (alates), workers, and or soldiers based on the requirements of the colony. Early colonies will not produce any alates as there is a population threshold that must be reached before the queen will produce them. Once they leave the nest in search of new territory, they usually land a few hundred meters away. The release of alates often coincides with fresh rainfall (Lewis, 2008) which is affected by the temperature and terms of season. Once male and female alate pair, they burrow into the nearest potential nesting area, develop a chamber for themselves and begin a transformation from alate to royal pair.

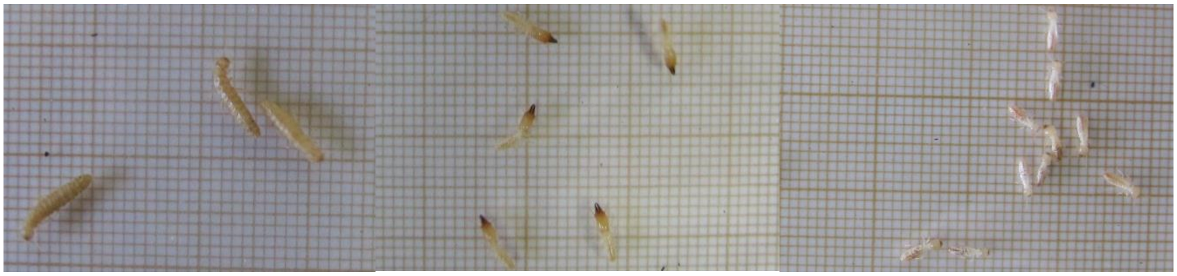


Figure 2.4 Some individuales of *Reticulitermes flavipes* (*ex. santonensis*) colony from Île d'Oléron island, France. left: supplementary (*neotenic*) reproductives; centre: soldiers; right: workers

2.5.2.3.2 **Soldiers**

Soldiers act to defend the colony from invasion by powerful jaws, or a bulb-like head that squirts a deterrent liquid. Their heads grow so large that they are incapable of feeding themselves and rely on the workers of the colony for this (Lewis, 2008)

2.5.2.3.3 **Workers**

Worker termites undertake the labors of foraging, food storage, brood, and nest maintenance and can result in invasion of timbers and crop fields. Workers expand and repair the colony, locate and prepare food and groom the queen. Since workers play such a crucial role in the health of a colony the vast majority of the termites in a colony are workers (Verma et. al., 2009).

2.5.2.4 **Subterranean termites of the genus *Reticulitermes***

The genera *Reticulitermes* (Holmgren) (Isoptera: Rhinotermitidae) are the major subterranean termite pests infesting wooden structures in the northern hemisphere, causing losses in the billions of dollars annually because of direct damage and termite control costs (Cameron and Whiting, 2007). *Reticulitermes* spp. are the most abundant naturally residing termites in Europe, with six described phenotypes (Clément et al., 2001). *Reticulitermes spp.* in Europe are known pests of urban structures and frequently pose threats to various agricultural crops.

Unlike in Europe and United States, the distribution of termites and their subsequent impact as an economic pest in developing countries Middle-east countries have not been reported (Austin et al., 2002). About the presence of *Reticulitermes* species in the Iran, although at first Weidner (1959) was unable to find *Reticulitermes* in Iran, but suggested that species from neighboring Iraq, may present a limited basis to their eastern distribution. Recently, some samples of *Reticulitermes* have been obtained from Iran. It would appear that there is a single distinct group of *Reticulitermes* which extend their range south towards the Persian Gulf and west towards Iraq. Iranian *Reticulitermes sp.* is genetically resembling Turkish *R. lucifugus* (Austin et al., 2006). European *Reticulitermes* species are test termites in EN 117 (2013) and EN 118 (2014) for determination of preventive action against subterranean termites. In our study we used *Reticulitermes flavipes* (*ex. santonensis*) which was collected from an island in the West of France.

2.5.2.5 **Current standard methods for termite test in European norm**

The exiting standard references for efficacy tests against termites are EN 118 (2014) and EN117 (2013), which are specialized for solid wood. So far, there is no standard termites test for WBC, particularly plywood, in European standardization system. Both of mentioned methods are force feeding test. It means just one sample is exposed to termites attack and they have no other option to choice. No choice tests are available as classic, standardized methods.

2.5.2.6 **Termites in Iran**

Investigations on the bionomics of termites in Iran are relatively scanty (Abivardi, 2001). In general, there are around 30 species of termite in Iran, which belong to four families (Ravan, 2010). Termites are distributed throughout the country and cause tremendous amount of damage to crops, trees, and buildings (Sedaghati Zade et al., 2013). The most common species of Iranian termites are included *Microcerotermes diversus*, *Amitermes villis*, and *Anacanthotermes vagans* that are classified as subterranean termites (Rahimzadeh et al., 2012). *Populus caspica* is one of the preferred host for these termite species in Iran (Ravan, 2010).

2.6 Wood preservation with low environmental impact

Today, environmental effect of the wood preservatives has attracted the attention of many researchers. Environmental performance and sensitivity of the wood preservatives are playing an increasing role in their development and use (Shmulsky & Jones, 2011). Future range of wood preservative will therefore be selected not only on the basis of criteria such as efficiency and cost, but also environmental impact, during service and even at the end of the lifetime (Hill, 2006).

CCA (chromium (VI)-copper-arsenic) have been the most used formulations for the treatment of wood and post treatment of WBC, particularly plywood. In 1997, about 80 percent of treated wood in United states utilized waterborne preservatives, of which 98 percent was CCA (Micklewright, 1998). CCA is very effective in extending the service life of the product. It is reported that CCA-treated wood lasts long sometimes until 60 years (Lebow, 2010). But CCA-treated lumber contains arsenic which may pose serious health risks, even after service time when the CCA treated wood becomes a waste (waste stream). As a result, in Europe and North America arsenic has been banned from most of the applications for preserved wood and wood products (Caldeira, 2010). There are several arsenic-free alternatives to CCA including Alkaline Copper Quat (ACQ), Copper Azole (CA), Copper Chrome Boron (CCB), Acid Copper Chromate (ACC), Copper Citrate (CC), and a number of others (Lebow, 2010). They rely on a high levels of copper as their primary biocide and some have co-biocides to provide preventing against copper-tolerant fungi (Lebow 2004). These alternatives have properties similar to those of CCA, but they release preservative components into the environment at a rate greater than or equal to that of CCA (Lebow, 2004). Although their main ingredients have lower mammalian toxicity than arsenic, but these systems contain high levels of copper, which can be toxic to aquatic life (Lebow, 2004; Shmulsky & Jones, 2011). Therefore, many studies are underway to replace metal oxides with more friendly biocides.

According to the above discussion, an environmentally favorable preservative must cover two main factors: (1) formed from more friendly ingredients, and (2) resistant to leaching.

Boron-based systems are good candidates for the future range of preservative formulations with lower environmental and health impacts and with broad spectrum fungicidal and insecticidal action (Caldeira, 2010; Lloyd 1997; Obanda et al., 2008). But, they are highly leachable from treated wood and WBC. The key to extending the use of borates to cover the entire spectrum of wood preservation is improving their permanence (Obanda et al., 2008).

2.7 Borate components and their applications

Borates are used in the manufacture of fiberglass insulation, detergents, fertilizers, flame retardants, and wood preservatives (Freeman et al., 2006). Borates have been used for over 60 years in Australia and Europe (Lloyd et. al., 2001). Boric acid (BA) H_3BO_3, disodium-tetraborate-decahydrate $Na_2B_4O_7.10\ H_2O$ (borax, BX), disodium-octaborate-tetrahydrate $Na_2B_8O_{13}.4H_2O$ (DOT), zinc borate $Zn(BO_2)_2$, and also some other boron compounds, belong to traditional preservatives for wood protection against wood-destroying fungi and insects in interior exposures (Kirkpatrick and Barnes 2006; Lloyd et al., 1998; Luo et. al., 2005).

Because of its favorable environmental characteristics wood preservation researchers have refocused on boron in the last two decades (Obanda et al., 2008). However, more recently (August, 2008) the European Commission decided to make an ATP – Adaptation to Technical Progress of Council Directive 67/548/EEC (the 30th ATP), and since then BA and BXare classified as reprotoxic category 2. These boron chemicals are classified as substances toxic for reproduction category 2 for both fertility and developmental effects. The directive apply to them the risk phases R60 (may impair fertility) and R61 (may cause harm to the unborn child). According to this restriction, concentration limits for BA and the BX are $\geq$ 5.5% and $\geq$ 8.5% respectively. However, borates have been registered by the U.S. Environmental Protection Agency (EPA) as wood preservatives. Also, they are still in use in Europe, but the concentration is limited.

Borates present many advantages for wood preservation. They are inexpensive, odorless, colorless, are non-flammable, effective against decay fungi and insects, water soluble and diffusible, and low toxicity to aquatic life (Clausen 2010; Freeman et al., 2009; Lloyd, 1997). Their high solubility in water allowing them to be introduced into wood by conventional methods like dipping- diffusion and or pressure treatments (Lebow, 2010). On the other hand, this advantage makes boron compounds easily leachable from treated wood and these woods are not suitable for outdoor application without any additional protection.

Borate preservatives are standardized by the AWPA (American Wood Preservers Association), but only for applications that are not directly exposed to liquid water. Borate-treated wood should be used only in applications where the wood is kept free from rainwater, standing water, and ground contact.

Currently borate component are using in wood preservation into three categories (Lloyd 1997):
- Decorative timber treatments and interior construction in the Asia Pacific area
- Formulation of exterior and remedial wood preservatives in Europe
- In construction, wood composites and pest control in North America

The greatest use of boron has been remedial treatments because of its high water-diffusion (Caldeira, 2010). Fused borate rods, glycol solutions containing borates, and remedial bandage wraps for poles are all being used for remedial treatment (Lebow et al. 2012). Since borates utilize the natural moisture in the wood to diffuse deeper over time, especially in wood having a moisture level of greater than or equal to 15 % (Lloyd et al., 1998).

2.7.1 Borates toxicity threshold against insects

Borates are considered more effective than copper and zinc (Freeman et al., 2009). Always a retention lower than copper and zinc is usually needed for the control of insects and wood-rotting fungi. To inhibit growth of the basidiomycetes fungi 200 mg/l of boron is necessary, but for copper sensitive fungi 640 mg/l and for copper tolerant ones up to 1500 mg/l of copper is required (Humar and Lesar, 2008). Borates have been proven effective against all known wood destroying organisms. Drysdale (1994) reviewed toxic threshold data of DOT for both fungi and insects (Table 2.1). Commercial retentions recommended for protection against termites are usually in excess of 1% (weight of chemical/oven dry weight of wood) BAE (Boric Acid Equivalent) equal to 4.5 kg/m^3 depending on timber density (Schoeman & Lloyd, 1998).
BAE is a standard unit of comparison of efficacy among borate compounds. For ease of comparison, boron compounds are often compared based on the BAE which obviously is the amount of BA that could be formed from the subject compound. In this study, all percentages used are weight/weight (w/w). For percent uptake of chemicals in wood, the percentage is based on the weight of chemical on the oven dry weight of wood.
Laboratory results indicated that borate was toxic to termites even at 0.24% BAE and caused significant termite mortality (Ahmed et al., 2004); but the minimum toxic threshold required to protect against termite attack and damage was >1.0% BAE. In an earlier study by Williams and Amburgey (1987) reported 0.3% BAE for adequate protection against *R. flavipes* in pine and >0.54% BAE is needed to protect against *C. formosanus* (Kartal et al. 2004).

Table 2.1 Toxic threshold data for DOT as determined by EN test (Drysdale, 1994)

Test, target organism	Retention	
	DOT, Kg/m^3	% BAE (w/w)
EN 113, Basidiomycetes	0.8	0.16
EN 20-2, *Lyctus*	1.0	0.20
EN 47, *Hylotrupes*	0.7	0.14
EN 49-2, *Anobium*	0.3	0.06
EN 117, Termites	5.6	1.12
EN330, L-Joint Field Test	0.8	0.16

As was observed, reference data for borates efficacy against termites are so different and vary from each study to another one. It is influenced by variations in test methodology, timber species and termite species. Generally around 1.0% BAE is necessary to provide protective effect against termites attack. For the control of wood borer beetles lower than this level is required.

2.7.2 Borates toxicity threshold against Fungi

The effectiveness of borates against basidiomycetes has been well documented in service and in laboratory studies by many workers. As yet, no wood decaying basidiomycetes have been reported to be tolerant against borates at normal preservative retention (Schoeman& Lloyd 1998). No brown rot fungi are known to have developed resistance to boron although this can occur with copper or arsenic containing preservatives (Drysdale, 1994). However, borates are effective against rotting-fungi but not against moulds (Reinprecht, 2010). Various studies have determined that 1.5 kg/m3 BAE is required to inhibit decay (McCutcheon et al., 1996).

In a recent study by Lesar et al. (2010) was reported 0.4 kg/m^3 of BA was enough to inhibit growth of *Antrodia vaillantii*, *Serpula lacrymans*, and *Trametes versicolor* on beech and spruce wood blocks. However minimum 0.8 kg/m^3 of BA were required to preserve wood against the most boron resistant fungal species. These results showed higher efficacy of BA against wood decay fungi in comparison to the data reported earlier.

2.8 Preservation of wood–based composites with borate components

Major problems with preservative chemicals used to treat composite products include leachability and toxicity. In any case, a preservative-treated wood composite product must provide adequate protection without sacrificing mechanical or physical properties. Borates are good wood preservatives with characteristics that make them well suited for use in WBC. The researchers have been working for several years to develop and evaluate wood composite materials containing one of a variety of inorganic borate chemicals as preservative or fire retardant or both.

The use of borates in wood preservation is investigated here with regards to different methods of preservation of wood composites which is described earlier in section 2.4.

2.8.1 Post treatment of finished products

It seems to be the easiest and the most practical method to preserve WBC. In this method preservative is applied on the post manufactured composites. It may perform by superficial treatment (spraying or dipping) or by pressure treatment.

The surface treatment of WBC is not sufficient. Since only the outside layer of the wood is protected, and the major part of the wood remains untreated (Shi & Walker, 2006). These afford an envelope of protection to the substrate and are mainly designed to provide short-term resistance to mold, decay and water intrusion. They are often utilized to protect building materials through transportation, storage and the construction process. Their major advantage is that they are relatively easy to apply and are very cost effective (Ross et al., 2003).

The use of surface treatments combined with diffusible preservatives such as borates offers deeper protection by forming a "penetrating barrier" of protection. In these systems, the face components remain at the surface where they are most needed to form a protective barrier against mold, insects, and surface moisture. The diffusible components penetrate to provide deeper protection against decay and insects (Smith & Wu, 2005).

The pressure post-treatment is not practical for all WBC. Since wood-based composites are difficult to impregnate, and impregnation can also result in shrinking, swelling and unwanted cracking of the wood or adhesive bond lines (Kralj et al., 2010). Hence, this method is possible when full phenolic glues such as phenol formaldehyde (PF) and other highly water resistant adhesive are used. In most cases treatment on post manufactured composites have done for veneer-based composites with traditional copper- based wood preservatives (Manning, 2002). However, the post-treatment with CA (Tascioglu & Tsunoda 2010, 2012) and ACQ (Tascioglu et al., 2013) improved durability of WBC to some extent but failed to provide full protection at exterior uses due to uneven distribution of the preservative in layer profile. Besides, the post-treatment has some adverse effects on dimensional stability, mechanical properties and requirements on re-drying (Khouadja & Barens, 2001).

As noted above, pressure treatment on assembled WBC in many casesis done by copper- based wood preservatives; however borates can be added as co-biocide to them. But we did not find any standalone borate formulation which is used for post-treated of WBC. With the exception of vapor boron treatments which offer another way to post treatment of WBC. Although, this method is promising but has not yet been commercialized (Smith & Wu, 2005). The methods involve exposing wood products to a vapor of volatile boron compound, trimethyl borate (TMB), which lead to hydrolysis of the ester and deposition of the active preservative ingredient BA in the wood (Murphyet al.,1993)

The treatability of wood (sapwood of *Cryptomeria japonica*) and wood-based composites (particleboard, waferboard, medium-density fiberboard, plywood) with vapor-boron was good, and the treated materials proved to be resistant to decay fungi and subterranean termites in laboratory bioassays. No difference in effectiveness was noted between vapor-boron and liquid-boron treatment of wood. A concentration of less than 1% BAE seemed sufficient to control biological attacks on WBC (Tsunoda, 2001). In another study, Decay test results of the wood-based composites well supported the applicability of the vapor-boron treatment. At a retention of 0.7% BAE, decay was satisfactorily suppressed, as the percent mass loss was less than 2% in any of the wood-based composites when the mass loss of untreated controls exceeded 15% (Turner, et al., 1990). Barnes and Murphy (2004) reported at 1% BAE by vapor-boron treatments which is satisfactory for protection in terrestrial applications; there are no negative effects on composite bending and tensile properties. Vapor-phase treatments of borates offer several advantages to conventional liquid treatments. Related to composite treatments is the fact that there is no liquid water to excessively swell the material. Impregnation problems arising from liquid tension and other interfacial considerations are eliminated.

2.8.2 Pretreatment of wood furnish

Treatment of wood furnish prior to gluing/pressing with borates is another technique that is used to protect wood composites against biodeterioration agents as well as fire. The homogenous distribution of chemicals on the thickness or layer profile of WBC and desirable retention are achievable with pretreatment of wood furnish. In this system adhesive compatibility with pretreated furnish is subject of several studies (Barnes 2012).

In 1958, Black published a paper in which he described the effects of pretreated veneers with BA and BX as fire retardant on bonding quality of different adhesives. In general, BX and BA treatment caused the most trouble in attempts to get a successful bond with urea glues. This difficulty may be ascribed to the relatively high basicity of BX and the high acidity of BA as well as a possible effect produced by the boron ion in urea-formaldehyde (UF) resins. BX, being quite alkaline in solution, increased the pH of the glue mixture well into the alkaline side, where the primary condensation product, dimethylol urea will remain in the liquid state for an indefinite period of time. BA decreased the pH of the glue caused a very definite shortening of the working life, which resulted in partially cured glue before pressure and heat were applied to the panel.

Laminated veneer lumber (LVL) made from beech wood veneers and pretreated with BA was tested for some mechanical properties (Colakoglu et al., 2003). The mean retention of veneers was 11.5 kg/m^3. BA treatment of veneers used in producing of LVL had no effect on the average MOE and bonding quality of PF adhesive; but it reduced average static bending strength.

The high retention of BA in this study was because of providing fire resistance. In many cases pretreatment of wood furnish with borates component is done in order to increase fire resistance. With pretreatment is possible to load desirable level of borates into the wood which is necessary to protect against fire (Bhatia, 2002). A minimum of 10% BAE is needed to provide fire resistance and meet the performance requirements for slow-burning materials (Tsunoda, 2001). Also, LeVan and Winandy (1990) stated that loading levels of more than 48 kg/m^3 of BX-BA are required to meet the ASTM E 84 (1998) Class I flame retardant classification.

Boron compounds are often considered good fire retardants because of their beneficial effects such as preservative effectiveness, neutral pH, and less impact on mechanical properties than some other flame retardant chemicals (Winandy et al., 1988).

In a recent study, Boron and phosphorus chemicals were used to increase fire resistance of plywood panels by pretreated veneers (Kartal et al., 2007). Although the BA and BX loadings were lower than the standard values, but all treated plywood panels showed good fire performance when compared to untreated panel. Plywood panels treated with BA and BX resulted in lower weight losses when compared to phosphorus fire retardant treated specimens in decay and termite resistance tests.

Increase in equilibrium moisture content (EMC) at high relative humidity has been a major problem in the use of boron fire retardant-treated lumber and plywood. It has been demonstrated that plywoods made of pretreated veneers with boron compounds (as fire retardant) had an increasing effect in EMC of panels (Aydin & Colakoglu, 2007; Aydin, 2014). This higher hygroscopicity may cause problems with appearance (discoloration), poor paint adhesion, surface finishing, migration and exuding of chemicals, and corrosion of metal fasteners (Winandy et al., 1988).

Together, these studies indicate that the use of borates for pretreatment of wood furnish is often done to protect against fire which may have somewhat negative effect on mechanical and physical properties. But they have less impact than some other flame retardant chemicals as well as they can provide protective effect against termites and decaying fungi. With some revise in glue formulation and with mixture of alkaline and acidic borates can lowered borates impacts on WBC properties.

2.8.3 In-line processes

A number of authors have studied the protective effects of borates addition when they apply with in-line process. In this approach borates can be apply by premixing with glue, as well as spraying to dry wood furnish before gluing.

In a study to increase durability of poplar LVL, BA was mixed with various concentrations (5 and 10% based on the adhesive solids) to MUF adhesive (Bridaux et al., 2001). Addition of BA did not influence bonding properties of the LVL. This study showed that under the applied conditions MUF is a good barrier against water and boron migration. After 15 days of leaching, 39% of initial boron was still present which could be enough to provide protective effect against fungal attack.

Similarly, it was tried to improve the fungicidal properties of glued laminated beams through the addition of BA to adhesives (Lesar et al., 2011). BA was added to the MUF adhesive mixture to achieve two different final concentrations of boron: 0.5 % and 0.1 %. The results of mechanical testing (shear strength and delamination) showed that the addition of BA to glue did not have a negative impact on the performance of the glued wood. On the contrary, some properties were even improved. But weight losses of the wooden lamellas bonded with adhesive enriched with boron were comparable to the control ones after expose to brown rot fungus. This could be due to large volume of wood to adhesive bond line. It seems this technique is not suitable for protection of glued laminated beams but may be possible for preservation of plywood or oriented strand boards (OSB).

Sometimes borates are mixed to the glue in order to modify glue characteristics. It has conclusively been shown that adding low amount of borates to urea glues did not statistically affect the mechanical strength of the plywood but also did reduce the free formaldehyde emissions from plywood panel (Çolakoğlu and Demirkir 2006; Sensogut et al., 2009).

It is worth noting that formaldehyde-based resins, however, have the advantages of superb bonding properties and are inexpensive. But they release formaldehyde vapors, thus causing health-related complaints (Kim, 2009). The reduction of formaldehyde emission from wood-based materials and the products made from them has been pursued by researchers in the adhesive and wood-based materials industries for many years. The International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) declared formaldehyde as a carcinogen in 2004 and the U.S. Department of Health and Human Services followed suit in 2011.

Usually borates are used as fire retardant with pretreatment methods where is possible to load desirable level of borates into the wood with less impact on the physical-mechanical properties of WBC. However, sometimes in-line process method can also be used to apply borate as fire retardant by spraying them directly to the dry wood furnish.

Effect of fire retardants on internal bonding (IB) strength and bond durability of phenolic-bonded structural fiberboard was evaluated by (Ayrilmis, 2007). BX, BA, and some phosphorus fire retardants were sprayed onto the fibers made from 50% pine and 50% beech woods at 2%, 4%, and 6% retention levels based on oven-dry fiber weight. The IB strength and bond durability of all the treated panels decreased with increasing chemical content. Same results were found for high-density fiberboard bonded by UF adhesive (Özdemir & Tutuş, 2013). In both studies, it was determined that borates enhanced the combustion resistance of the panels to varying degrees by spraying chemicals onto the fibers.

In fact negative effects of borates addition on physical and mechanical properties appear when plenty of these materials are used as fire retardant.

Currently, the most common preservative used on wood plastic composites (WPC) and OSB in North America is zinc borate (ZB), applied either as a powder or an emulsion/dispersion. ZB is far less soluble and can be evenly distributed on the thickness of products by in-line processes (Laks, 1999). However, when combined into a wood composite material, leaching under direct water exposure may still occur (Lee et al., 2004). ZB can be applied in both premixing with glue or spraying to dry wood furnish in the blender. ZB are preferred in wood chip applications due to their ability to dissolve slowly and their compatibility with the resin systems used.

The effect of incorporation of ZB and calcium borate (CB) into OSB was investigated against decay and mold fungi. ZB or CB was sprayed on the strands along with PF resin in a blender through different spray nozzles. The target loading levels for ZB and CB were 0 (control), 0.5, 1.0, 3.0, and 4.5 wt % (Xu et al., 2013). The results showed ZB and CB into OSB provided a suitable protection against brown-rot fungus, even at the low loading level (1% BAE). Untreated OSB was most susceptible to mold growth. However, borate treatment effectively prevented the mold growth, and the effect increased with the increase of borate retention level.

Wu et al. (2002) reported static bending properties of the OSB were affected little at room condition by the added ZB. The IB strength was, however, generally smaller at the higher borate loading levels. It was shown that thickness swelling increased with increased borate content, especially for calcium borate. Laboratory no-choice termite tests indicated that both ZB and CB modified OSB resisted Formosan termites well. The evidence presented in this section suggests that termite-resistant structural OSB with desired mechanical and physical performance could be successfully developed with a right combination of wood species, borate type and content, and other processing variables. Of particular importance, it was noted that borates with a smaller particle size helped reduce sample thickness swelling and leaching rate.

The effect of particle size in reducing leaching rate is well documented by Clausen (2012). For instance, Nano-zinc oxide particles were shown to be leach resistant, when compared to ZB. Protection systems using Nano-materials are being developed to enhance the durability of wood-

based composites through improved resistance to biodeterioration, reduced environmental impact from chemical leaching, and improved resistance to ultraviolet degradation (Clausen, 2012).
The incorporating ZB into the WPC has been well responded by industry in order to increase natural durability. The effect of ZB and sodium/calcium borate addition was investigated against a brown rot fungus (Simonsen et al., 2004). The preservatives were added to the mixture as powders at 0.0, 0.5 or 1.0% (w chemical/ w wood). At either treatment level, weight losses were negligible with ZB and tended to remain below 1% with Na/Ca B. Similarly, it was reported that the addition of ZB at 1% retention level significantly decreased weight losses of WPC when exposed to laboratory decay and termite tests (Tascioglu et al., 2013).
The mechanical properties of ZB-treated poplar WPC was studied by Badritala et al. (2013). In this study ZB was applied with two methods: (1) pretreatment of wood flour with ZB solution, and (2) adding ZB as powder into the mixture during WPC making. The concentration level of the ZB was designed to be 1%, based on the weight of oven-dried wood flour. Specimens containing the ZB showed lower flexural, tensile, and impact strength compared with the untreated specimens. The composite made with ZB-pretreated wood flour exhibited the same mechanical properties as the composites made with ZB-in-process-treated wood flour; however there were statistically significant reductions in flexural modulus and tensile strength of ZB-pretreated composites compared to ZB-in-process treated ones.
Major problems with borate preservatives used to treat composite products include leachability and their impacts on physical-mechanical properties. Borate-treated composite products are susceptible to leaching and are not usually rated for ground exposure. Borate leaching from WBC under harsh exposure conditions may be problematic and further study is needed in this section. On the other hand over-use of borates will adversely affect physical-mechanical properties.

2.9 Borate fixation in wood

Probably any time the role of boron as a wood preservative is discussed, it is referred the fact that boron is not fixed chemically to wood. Although boron has many advantages as a wood preservative and fire retardant, this chemical performs poorly in leaching exposures. Over the years, there have been various tests with boron formulations and other chemicals in order to improve the durability of wood preservative treatment. But the problem of high leachability of boron has not yet been completely solved.
The key to extend the use of borates to cover the entire spectrum of wood preservation is improving their permanence in wood while retaining efficacy by retaining limited mobility of the borate (Pizzi and Baecker 1996). Previous studies show that while fixing boron may prevent leaching, it may lock the boron resulting in loss of biological efficacy (Lloyd et al., 1990). Borates have favorable environmental characteristics, but their high susceptibility to leaching is the main obstacle to the widespread use of boron as a major component of broad- spectrum wood preservatives (Caldeira, 2010).Three in-depth reviews have been published recently about borates as well as their fixation: Caldeira (2010); Freeman et al. (2009); Obanda et al. (2008).

Obanda et. al. (2008) reviewed research over the last two decades in laboratories around the world and classified all strategies employed into fifteen categories. For each strategy, resistance of the treated wood to wood destroying organisms, resistance to leaching, and potential applications were discussed in there. While little or no commercialization has taken place with most of these fixed borate systems (Freeman et al., 2009). There are still many open questions about these systems and a long way to go in regard to their maturity. The Table 2.2 is a brief overview of fixed systems reviewed by Obanda et al. (2008) and a brief description is given for each. So far, other methods have been added to this list, as well as some modifications have been done on existing methods. However, many important results have been achieved in the field of borates stabilization. But the problem of high leachability of boron has not yet been completely solved.

Common point of these methods is incomplete fixation of borates. For example, leachability of zinc borate-modified OSB panels was investigated by exposing edge-sealed OSB samples under running water at 31^{o}C for 8, 24, 72, and 216 h. The results from leached samples were compared with those from the unleached controls. In fact, all of the borate was removed during the leaching periods. Boron leaching of the modified OSB occurred upon the initial water exposure, and the leaching rate decreased as the leaching time increased. The glue-line washing within OSB due to thickness swelling of the test samples under water and decomposition of the borate to form water-soluble BA were thought to be two possible causes for the observed leaching (Lee and Wu, 2007).

Another example for failure of the borate stabilization is reported by Humar et al., (2004). Whereas, CCB is presented as a fix type alternative for CCA (Lebow 2010), but leaching of boron from the CCB-treated wood samples rendered them susceptible to decay by the copper tolerant fungi after leaching experiments. Also it was reported that essentially 100% of the boron was lost from CCB formulation after only a few days of leaching, regardless of the different treatment methods (Nair, 2006).

The methods mentioned in Table 2.2 have some advantages and disadvantages. Depending on the application one of these methods can be selected. Some of them are very cost effective and applicable but have protective effect only for a short term exposure to the water. Some others are more effective but the high cost of them and complicated processes hinder the commercialization of those.

Recently, some initiatives have been done to the methods mentioned in Table 2.2. Palanti and Feci (2013) used commercial silica Nano dispersions, instead of other compounds of silica, to guarantee the fixation of BA to the wood. The results were promising, especially those concerning boron fixation and efficacy against decay fungi through laboratory tests. The loss of BA was only 23.0% after EN 84 leaching periods. Some formulations and retentions gave a durability class 1 (very durable) according to EN 350-1 (1995), with an expected service life exceeding 25 years.

Table 2.2 System proposed for reducing boron leaching over the last two decades were reviewed by Obanda et al. (2008).

Item	System	brief description
1	Surface treatments	Coating boron-treated wood with layers of varnish, resins and, hydrophobic wax to hinder moisture uptake
2	Envelope treatment (over- treatment)	over-treatment of borate-treated wood with creosote
3	Wood bulking resins and water repellants	Physically restricting water access in wood by impregnating it with hydrophobic agents limit boron mobility without interfering with its bioactive nature.
4	Organo boron compounds (boronic and borinic acids)	Aromatic boronic acids have leach resistance from wood due to the higher possibility of them interacting with the aromatic subunits of lignin and restricting access of water to the boron.
5	Precipitation of organo soluble salts within wood	chemical complexion of a borate compound with an agent capable of forming a water-insoluble complex upon dehydration in wood
6	Combination of biocides and non- biocidal chemicals	Non-biocidal additives may give wood greater and/or broader protection than achieved with only the biocide. Treatment of wood blocks with borates and N`N 1,8-naphthalyl hydroxylamine solutions in sequential processes reduces the susceptibility of boron to leaching
7	Metallo-borates	ZB incorporated into composites offers much better leach resistance copper borate complexes that formed in the wood were responsible for the long term protection. Also wood can be treated with inorganic borates and metal salts in two steps to form insoluble precipitates within wood.
8	Ammoniacal and amine metallo-borates	Solutions of metallo-borates and acetic acid or ammonia can be chemically fixed in wood Also metal-free systems formulated with quaternary ammonium carboxylates and quaternary ammonium borate in an aqueous solvent displayed greater resistance to leaching than stand-alone borate systems.
9	Stabilized boroesters	Hydrolytically stable borate esters with biocidal properties include trialkyl amine borates, trialkanolamine borates (borate salts of triethanolamine or triisopropanolamine), monoalkanolamide borates, and esters of carbamates containing polyhydroxyl substitutes on the nitrogen atom. The esters are more resistant to leaching than soluble borates.
10	Protein borates	BA can be partially fixed to timber by forming an association with animal and vegetable proteins, which is then insolubilized by heat induced coagulation to form complexes and acid–base salts. This mechanism while retarding leaching leaves small amounts of boron free to diffuse and exercise activity.
11	Tannin auto condensation	Tannins can fix biocides because of their excellent chelating properties. BA is used to induce autocondensation of flavonoid tannins, leading to the formation of a network of solid autocondensed tannin throughout the wood structure to which the borate is partially fixed.
12	In situ polymerization	The wood cell wall is impregnated with monomers which are then polymerized in situ resulting in swelling of the cell wall which increases the dimensional stability and water penetration of wood. For instance, treated wood with BAand then impregnated with vinyl monomers caused five times less boron release compared to that solely treated with BA
13	Vaporization of organic boron compounds and BA	Vapor boron treatment of wood composites by trimethyl borate integrates the drying and treatment processes. Vapor treatment with BX in a closed chamber without mechanical compression to wood resulted in increased leach resistance of boron
14	Boron-silicates	Soluble alkali metal silicates have been employed as agents to reduce boron leaching in numerous studies. Silicic acid and BA impregnated into wood in a single step displayed high water resistance.
15	Physical modification of wood (compressive deformation)	Compressive deformation of wood is achieved by heating under certain conditions. Compression to a permanent state is densification and reduces the volume of void spaces in wood for liquid uptake. As a result, it decreases borates leaching.

However, extensive research has been conducted with varying anhydrides and water repellants. But Terzi et al. (2011) evaluated a commercial water repellent compound to decrease boron leaching from treated wood with DOT. There were two different processes for preservative treatments: double treatments and single treatments. In double treatments, wood specimens were first treated with DOT at 0.1, 0.5 and 1% (% m/v) concentrations, and then treated with a commercial water and oil repellent compound called FORGUARD. The compound contains 3.6% dipropylene glycol monomethylether, 12% solids and 78.4% water in its formulation. In single treatments, DOT was mixed with the compound yielding 0.1, 0.5 or 1% (% m/v) DOT concentrations. All boron was leached out from DOT-only treated wood specimens; however, less boron release was seen in the specimens containing water repellent compound. Nearly 50% of boron remained in the specimens treated in double process after 10-day leaching according to Japanese Industrial Standard (JIS) K 1571 (2004).

Most Recent study on borate fixation was carried out by Salman et al. (2014) who developed a new wood treatment by combining boron impregnation and thermal modification. Prior to heat treatments wood samples were treated with BX and two additives to reduce boron leachability. The additives were water soluble polymerizable polyglycerol derivatives including Polyglycerol/maleic anhydride adducts and Polyglycerol methacrylate. The results showed boron and thermo-modification in the presence of different additives allowing the improvement of the resistance of boron to leaching with water.

One of the borate-based methods to preserve WBC is addition of boron compounds into the glue line. It has been demonstrated that addition of BA to the MUF adhesive significantly reduces boron leaching from LVL panels. The results shown after 15 days of leaching, 39% of initial boron was still present which could be enough to provide protective effect against fungal attack (Bridaux et al., 2001).

Recently mechanism which was described by Pizzi & Baecker (1996) about interaction of boron compounds with tannins (eleventh item in Table 2.2) was developed , and up to now many studies have been carried out to define the properties of these innovative formulations. Further work revealed that hardening of condensed tannins by hexamethylenetetramine (hexamine) in alkaline environment, when BA is complexed onto the network; markedly slow down the leaching of boron (Thevenon et al., 2010 and 2009). This formulation showed significant results, and it was further studied to extend their protection properties and to their possible applications in outdoor buildings (Tondi et al. 2012a; Tondi et al. 2012b; Tondi et al. 2012c).

Borates stabilization system with chelating properties of condensed tannins seems attractive to preserve WBC, particularly plywood. This system can be used in particular for both pretreatment and in-line processes. Condensed tannins as an eco-friendly base of resin are excellent renewable alternatives to overcome on formaldehyde-based wood adhesives drawbacks (Pizzi., 2006). In this regards we became interested after reading literatures about condensed tannin properties for borates fixation. And an idea took shape to use this system for environmentally favorable protection of plywood against biodegradation. At first it was decided to use this system with in-line process (glue line treatment) with concentrated solutions of tannin/hexamine-BA. Secondly, the diluted solution of this system was considered to use in pretreatment process for pre-impregnation of veneers.

The remaining part of current chapter will give more information and literatures reviews about this system and tannin based adhesives.

2.10 Condensed Tannin and its application

The tannin compounds are widely distributed in many species of plants, where they play a role in protection from predation, and perhaps also as pesticides, and in plant growth regulation. Tannins are found in leaf, bud, seed, root, and stem tissues of plants. Chemically, they are mainly phenolic compounds. While historically tannins have been associated with the preservation of hides to leather. Recently, with growing demand for use of naturally derived materials, more new application are found for tannins. One area suited to this is the development of natural tannin adhesives in wood-based composite manufacture (Pizzi 2006).

It is commonly accepted that tannins are divided into two main classes (Pizzi 2003): hydrolysable tannins and condensed tannins.

The hydrolysable tannins are mixtures of simple phenols. As the name indicates hydrolysable tannins are hydrolyzed by weak acids or weak bases to produce carbohydrate and phenolic acids such as gallic acid or ellagic acids (Figure 2.5). The lack of macromolecular structure in their natural state, the low level of phenol substitution, their low nucleophilicity, limited worldwide production, and higher price somewhat limit chemical and economical interest in these.

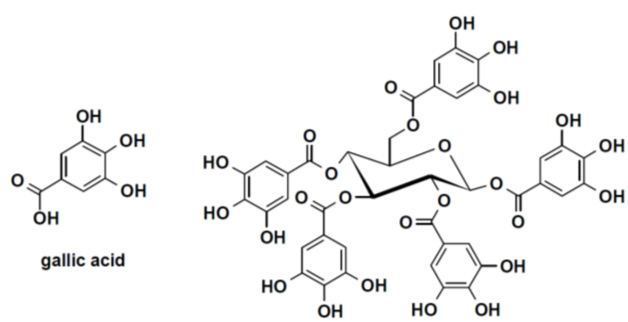


Figure 2.5 Schematic representation of a hydrolysable tannin molecule formed with gallic acid units (Pizzi 1994).

Condensed tannins, on the other hand, constituting more than 90% of the total world production of commercial tannins (200 000 tons per year), are both chemically and economically more interesting for the preparation of adhesives and resins. Different types of condensed tannins are formed from flavonoid units (Figure 2.6). Condensed tannins are abundant and readily available in the wood and bark of various trees. The major species from which it can be obtained are *Acacia* (wattle or mimosa bark extract from South Africa), *Schinopsis* (quebracho wood extract from South America), and *Pinus radiata* (Radiata pine bark from Australia) (Kim 2009; Van Langenberg et. al., 2010). Condensed flavonoid tannins are used to obtain the low formaldehyde emission levels required for environmental-friendly adhesives (Pizzi, 1994). Recently, formaldehyde has been classified as a probable human carcinogen (Siemiatycki et al., 2004) and its use could be limited in the near future (Bertaud et al., 2012).

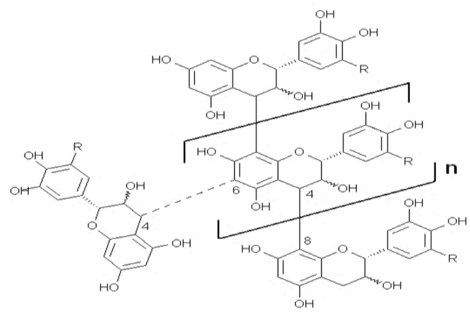


Figure 2.6 Schematic representation of a condensed tannin formed with flavonoid units (Pizzi 1994)

Condensed tannins can be used in the manufacture of adhesives with two approaches: polycondensation reaction or autocondensation reaction.

2.10.1 Polycondensation with aldehydes or non-aldehyde hardeners

The attractiveness of using tannins in wood adhesives can be derived from their similar reactivity and cross linking chemistry with formaldehyde as that found for phenol- and resorcinol-formaldehyde systems. This commonality in reaction chemistry has been the main stay of tannin use in wood adhesives (Van Langenberg et al., 2010). The reactions of tannin with formaldehydes or other aldehydes have been used extensively and it is known as polycondensation reaction (Pizzi 1994). The tannin-formaldehyde adhesives in production of WBC has been commercial for several years and are used in a number of countries (Pizzi 2006; Pizzi 1994). The exterior-grade WBC bonded with tannin adhesives is only achievable by polycondensation reaction of tannin with aldehyde hardeners. The reaction of tannins as phenolic materials with aldehyde has always traditionally yielded weather- and boil-proof networks (Pizzi et al. 1995; Pizzi 1983). Since the aldehyde cannot be liberated from this system, tannin based adhesives, on the other hand, have very low formaldehyde emission (Pizzi, 2006).

Another achievement in the tannin based adhesives is mechanism of hexamine as a non-aldehyde polycondensation resins hardener in alkali environment (Pizzi, 1994). Hexamine is considered as hardener which is not at all a formaldehyde-yielding compound. Particularly, when it is used as a hardener for a fast reacting wood species; it does not decompose to formaldehyde and ammonia (Kamoun et al., 2003; Kamoun and Pizzi, 2000). Formaldehyde emission measured in the large chamber test has been shown to be so low as to be limited exclusively to that generated by the heating of wood itself (Pizzi 2006). The panels obtained with tannin-hexamine adhesives, depending on the conditions under which they are manufactured, can satisfy both interior- and exterior-grade standard specification requirements. It was capable of yielding interior grade particleboard with slower reacting tannin such mimosa and quebracho with hexamine. But with faster reacting pecan/pine industrial tannin and with some revising in the pressing condition, exterior-grade particleboard was achievable by tannin-hexamine adhesives (Pizzi et al., 1997).

2.10.2 Autocondensation reaction without hardener

The reactions of tannins which are taking place in the absence of external hardeners and involves opening of the rings under alkaline and acidic conditions is referred to tannins autocondensation (Pizzi, 1994). This approach uses a unique facet of condensed tannin chemistry in which the tannin oligomers are promoted to self-polymerise forming a cross-linked polyphenolic network. Autocondensation rate of the various tannins is different. Pizzi et al. (1995) has reported mimosa and quebracho tannin are slower tannin compared with pecan nut tannin which has ease fairly rapid autocondensation reactions without need for catalyzer. Pecan nut tannin and pine tannin need only lignocellulosic induced autocondensation to give excellent interior grade particleboard. But mimosa or quebracho tannin adhesive based on autocondensation reactions need more pressing time and indicates low IB because of their slow hardening rate.

It was reported that the autocondensation to gelation of various tannins is inducible by weak Lewis acids such as silica, BA and aluminum chloride (Meikleham et al., 1994). In fact, Lewis acids act as hardener or catalyst for tannin autocondensation (Pizzi et al. 1995b). The problems associated with slow reaction tannins can be solved with Lewis acids-based autocondensation systems which lower pressing time and also upgrade IB (Pizzi et al. 1995a). The tannins hardened by autocondensation approach, induced either by lignocellulosic surface or Lewis acids, only yielded bonds of interior-grade quality (Pizzi 2003; Pizzi 2006).

The studies were conducted to accelerate the autocondensation reaction of tannins led to the creation of mechanism for fixing BA (as weak Lewis acid) in the wood.

2.11 Borates fixation with condensed tannin and its promotion over time

From the previous section, BA (or other weak Lewis acids) induces autocondensation and hardening of polyflavonoid tannins. The mechanism of this reaction is based on the Lewis acid acceptance of electrons from the ether oxygen of the flavonoid unit pyran ring with concurrent and consequent facilitation of base induced heterocycle opening. The reactive site so formed is blocked, by the charge of the Lewis acid counterion, from undergoing the intramolecular bond rotations generally associated with intramolecular rearrangements of the unit. The effect hence addresses the subsequent condensation of the reactive site formed away from internal rearrangements and towards condensation with a flavonoid unit in another polymer chain. This leads to cross-linking and networking of the material to a hardened state (Meikleham et al., 1994; Pizzi, 1994) (Figure 2.7)

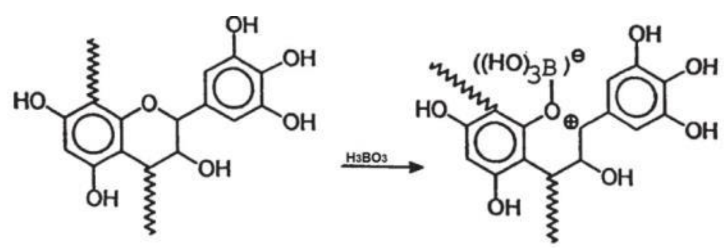


Figure 2.7 schematic representation of BA effect on opening of pyran cycle and the formation of very reactive site (Pizzi & Baecker, 1996)

In this regard Pizzi and Baecker (1996) described a mechanism in which BA was used to induce autocondensation of condensed tannins. Then the BA could partially fix to the network by the autocondensed tannin. This system conserved sufficient mobility to maintain BA preservative action. The system is based on slowing down the potential leaching of boron from the wood without completely stopping its mobility.
The ministakes *Pinus radiata* samples (100 × 10 × 10mm) were imperginated in two steps with an aqueous solution containing 0.6% BA and a 2.5% aqueous solution of tannin. The commercial tannin of pecan (*Carya illinoensis*) nut pith tannin was used to make solution. Some of the ministakes were treated first with the BA solution, then with the tannin solution and drying at 105°C. Other ministakes were treated first with the tannin solution followed later by the BA solution. The accelerated termite field test results indicated that this environment friendly treatment increases permanence of boron in the wood with consequent preservative durability between three and six times. The better long term results were clearly obtained by treating with boron first and tannin second. Comparison with the controls clearly indicated that leaching of the BA was greatly reduced and retarded by the treatment, but leaching still occured. Finally it was concluded that this treatment does not appear suited for ground contact applications but only for aerial, non-ground contact ones.
Thereafter, others found composites panels (hemp shaves isolator boards) bonded with the mimosa tannin- hexamine adhesive show better IB when BA was added to the glue as biocides (Theis & Grohe, 2002). The addition of BA, also, provided good preservative effect against mold fungus even after a short-time leaching test. Nearly 45% of the boron was left in the composite after 4 days leaching in the best treatment. The strength of mimosa-hexamine systems was not capable to reach exterior application quality. The IB values were drastically decreased in leached samples. In another study, the decay resistance of wood products bonded with cornstarch-tannin adhesive was studied by BX with two approaches: (1) glue line treatment and (2) pretreatmet of wood veneers (Moubarik et al., 2009). For glue line treatment, BX was added in proportions of 0.5%, 1% and 2% w/w to the cornstarch-tannin adhesives. The results showed that the mechanical properties of cornstarch-tannin adhesive decreased significantly when the concentration of BX was increased. The authors stated this may have been due to a decrease in pH value of the adhesive or to an effective lowering of the molar ratio due to the presence of reactive material, like the tannin, or to the well-known marked effect of decrease in viscosity that BX has in all starch adhesives. The impregnation of wood veneers with BX did not have negative effect on the mechanical properties of composites. The samples made from wood impregnated with BX at 0.5% and 1% (w/w) aqueous solution have the same shear strength values. Since the cornstarch-tannin adhesive is intended for indoor applications; hence, a relatively lower retention load is needed. So, wood impregnated with BX at 0.5% (w/w) was selected as the best.
Thevenon et. al. (2009) formulated another tannin resin-boron wood preservative. The several features were coupled together to increase performance of method which was described by Pizzi and Baecker (1996). The hardening of tannin by hexamine (polycondensation hardener) was

combined with BA (autocondensation inducer) and these was further coupled with a protective unsaturated oil heat treatment to further improve wood water repellence, consequently less boron leaching. For this, beech (*Fagus sylvatica*) wood specimens were treated with a number of preservative solutions. Tannin was prepared in three concentrations (10, 20, and 30%) and 6% hexamine was used based on the tannin solid as hardener. BA was used 5% based on total tannin solution. Half of the treated specimens were leached by daily exchange of water for five days.

The boron leaching from treated wood with tannin+ BA solution (formulated by Pizzi and Baecker, 1996) was still very high and the results of fungal test were not very different from the untreated controls after leaching. But the samples treated with tannin+ BA+ hexamine and with tannin+ BA+ hexamine then dipped in hot sunflower oil gave interesting results. The percentages of weight loss after fungal test for leached and unleached specimens were very low. Hence these formulations had a remarkably effective preservative action after leaching. The results showed that there is no great difference between the mass loss after fungal attack when oil is present or absent.

About reducing impacts of this system on the boron leaching, Thevenon et. al. (2010) stated that the resinification of the hydrophobic tannin + hexamine system greatly reduces leaching of the BA. The BA is then still most non-covalently bonded to the tannin resin but retains sufficient mobility that allows it to work as a fungicide.

The efficacy of tannin in fixing boron in wood was studied further by (Tondi, et al., 2012a). The various modifications of the tannin-boron based formulations were studied, with particular attention being paid to the leaching of boron by comparing two methods of leaching and fungal as well as termite resistance. Beech (*Fagus sylvatica*) and Scots pine (*Pinus sylvestris*) wood specimens were treated with a number of experimental wood preservatives which is described in Table 2.3. Some additives were used to modify tannin-boron formulation and lower BA content were mixed to the solution than the earlier studies conducted by Thevenon et al. (2010, 2009). Two different kind of leaching were applied on the treated samples: (1) daily exchange for five days and (2) EN 1250-2 (1995).

Table 2.3 Description of tannin-boron formulations used by Tondi et al. (2012a)

Tannin w/w %	Boric acid w/w %	1-Methyl-2-propanol w/w %	Other addatives w/w %
10	0.5	1	-
15	0.75	1	-
20	1	1	-
20	1	-	-
20	0.6	1	-
20	1.4	1	-
20	1	1	1% of H_3PO_4
20	1	1	1% of $(NH_3)_2HPO_4$

The boron releasing study during the leaching showed that the boron is leached out mainly at the beginning of the leaching process. This phenomenon was explained based on an incomplete polymerization of the tannin resin. These flavonoid oligomers and the free BA will be the first to be leached out. This also occurred in the subsequent leaching but with a decisive decrease in intensity. The leaching was more evident when a lower concentration of tannin was applied. The leaching behavior of boron in tannin-boron wood preservatives is shown in Figure 2.8 for beech wood samples according to daily exchange for five days leaching procedure. The biological tests showed extremely high resistance of the leached samples against fungi (*Coriolus versicolor* and *Coniophora puteana*) and termites (*Reticulitermes santonensis*). Furthermore, solid state 13C-NMR analysis of the tannin resin indicated that boron was covalently fixed to the tannin-hexamine network.

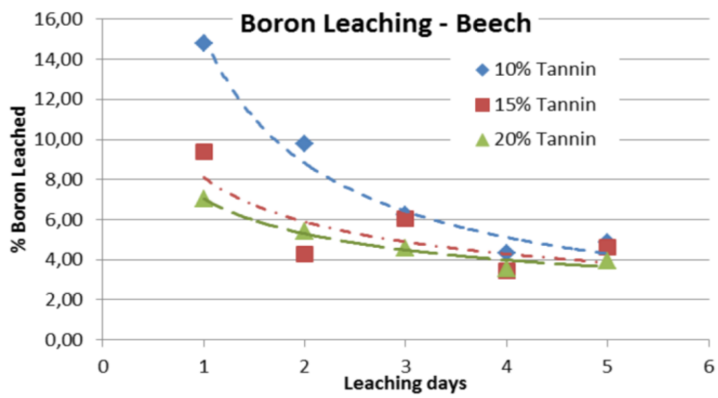


Figure 2.8 percentage of boron released by tannin-boron treated beech samples monitored every day for the 5 days of leaching (Tondi et al., 2012a).

In another study (Tondi et al., 2012b) mechanical and fire-proofing attributes of Scots pine and beech specimens treated with tannin-boron formulations were studied. Tannin impregnation solutions were prepared with 10% and 20% w/w mimosa extract. 6.0% by weight of hexamine was added as the crosslinking agent. BA and phosphoric acid (5% w/w) were added in the formulations to investigate the behavior against fire. The tannin-hexamine formulations reticulated into the wood structure improved the strength of the treated specimens. The treated samples which underwent compression, bending, hardness and gluing tests showed improvements of on average 20%. A positive effect on fire-resistance was shown when wood was treated with tannin formulations. The fire-proofing properties of the resin were upgraded with adding boron and phosphorus.

The positive outcomes of the previous studies on the tannin-boron formulations caused further study on this new environmental wood preservative (Tondi et al., 2012c). Scots pine sapwood specimens were treated with tannin impregnation solutions at 10% and 20% w/w mimosa extract. The pH of these solutions was corrected with NaOH to a pH of 9.0. Then 6.0% of hexamine (w/w tannin) and 5.0% (w/w tannin) of BA were added at the end of the preparation.

The results showed the amount of tannin and boron that leached out with EN 84 method was quite high compared to the mild EN 1250-2 leaching test. In total, EN 84 removed up to approximately 35% and 20% of the original tannin (and consequently boron) that was originally retained at 10% and 20% tannin solution, respectively. The mortality rate of the larvae of

Hylotrupes bajulus was 70% , 3.3%, 10%, and 30% in untreated, unleached treated, leached EN 1250-2, leached EN 84 at 20% tannin concentration, respectively.

The study of dimensional stability showed that the treated samples are more sensitive to changing moisture conditions and stronger internal stresses. The continuous change in moisture and temperature that occurs during the weathering caused crack more often and with deeper cracks than the untreated specimens because of a higher swelling coefficient. The tannin-impregnated samples had more stability against discolorations than the untreated ones even if the weathered samples tend to turn grey.

In the last study on the tannin-boron formulation Tondi et al. (2013) evaluated impregnation of Scots pine and beech with tannin solutions, with particular attention being paid to the effect of viscosity and wood anatomy in wood infiltration. It was seen that in the case of waterborne tannin solutions, the penetration is quite easy for beech while the treatment of Scots pine needs more attention. When formulations with higher concentration were applied to Scots pine, the complete impregnation rate was not achieved. Whereas there was no problem with 10 % low viscosity solutions. Microscopic analysis showed that penetration in Scots pine occurred longitudinally through tracheids with open bordered pits and across radial direction through parenchyma rays. Beech was almost exclusively penetrated in the longitudinal direction through large and easy accessible vessels (Figure 2.9).

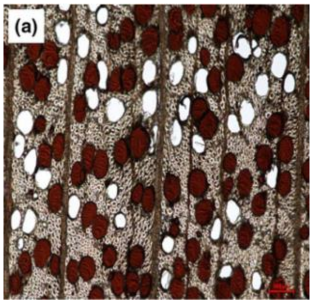


Figure 2.9 Cross section of impregnated beech at ×10 magnification (Tondi et al. 2013).

2.12 Conclusion for literatures reviews

According to what is being said, tannin-based formulations are suitable for a new generation of environment-friendly wood preservatives. So far, no research on the use of this approach was carried out to protect wood-based composites. It looks there is high-potential in this system to preserve WBCs against biodegradation. This dissertation is the first study on the use of tannin-boron to protect plywoods with two approaches: Glue line treatment and treatment of wood veneers.

CHAPTER 3: Material

This chapter describes the experimental design and manufacturing methods of plywood panels.

3.1 Design of experiments

The experiments to produced plywoods with treatment based on associations between boric acid (BA) and tannins were organized according to two approaches.

For the first approach, it was decided to use the tannin-BA as glue for bonding veneers together.

For the second approach, wood veneers were treated with different formulations of tannin/BA prior to gluing/pressing. Then, theses veneers were bonded together with MUF (Melamine Urea Formaldehyde) adhesive.

The following diagram (Figure 3.1) shows the design of experiments in this study. Poplar plywoods were made in Iran with quebracho tannin and beech plywoods in France with mimosa tannin. Both wood species were used for each approach. Throughout this dissertation, the term glue line treatment will be used to refer to the first approach and veneers treatment to the second approach.

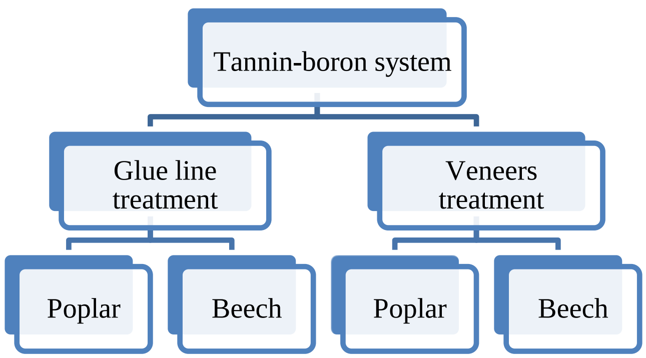


Figure 3.1 Diagram of experimental design

3.2 Wood veneers

The veneers of two woody species, poplar and European beech, were selected to make plywoods. These woods were chosen because of their low durability against biodegradation. Poplar and beech, on the other hand, are easily accessible in Iran and France and play very important role in wood supply.

Rotary-cut beech (*Fagus sylvatica*) and poplar (*Populus deltoides*) wood veneers with nominal dimensions of 450 mm × 450 mm × 2 mm (length × width × thickness; L×W×T) in air dried condition were selected to make plywoods. In this study the air dried conditions refers to conditioning in roofed and uncontrolled environment for at least one month. The moisture content (MC %) of the veneers was determined by using 10 replicate specimens with the following equation:

$$Equation\ 1 \qquad MC\ (\%) = \frac{m_1 - m_2}{m_2} \times 100$$

Where m_1 is the weight of the veneers in air dried condition and m_2 is the weight of the sample after oven drying until the constant weight.

Constant oven dry weight was considered as having been reached when the results of two successive weighing operations, carried out at an interval of 4 h, do not differ by more than ± 0.05 g. Throughout this dissertation, the term constant oven dry weight refers to this description.

The moisture content of the veneers was 7 ± 1% for poplar and 8± 1% for beech prior to gluing.

The veneers were classified visually based on observable defects, such as cracks and knots. Only veneers without any defect were visually selected.

3.3 Tannins

The tannins of quebracho and mimosa were used in this study. They are most abundant commercial tannin available in the market and both of them are classified as condensed tannins. The reacting rate of these tannins are more and less similar and are considered as slow reacting tannins compared to pine and pecan nut tannins (Pizzi et al., 1995). Quebracho tannin is extracted from *Schinopsis spp.* wood in South America and mimosa tannin from *Acacia* spp. bark in South Africa.

In this study, the commercial condensed tannin of quebracho wood (*Schinopsis balansae*) extracted in Argentina and the mimosa barks tannin (*Acacia mearnsii*) sold under the name Mimosa OP and supplied by the company SilvaChimica (Italy, origin Tanzania) were used.

3.4 Plywoods with treated glue line

The tannin/hexamine adhesives were made at different tannin concentrations and by adding varying amount of BA for gluing beech and poplar veneers. Also, polymeric 4,4′ - diphenylmethane diisocyanate (PMDI) resin was added at 20% based on the tannin solids to the adhesive. Sometimes PMDI is needed in a small amount to enhance the quality of the basic adhesives such as tannins (Pizzi 1994).

3.4.1 Preparation of the tannin adhesive

3.4.1.1 Quebracho tannin adhesives

The main ingredients of the adhesives include: (1) quebracho tannin; (2) Sodium hydroxide (NaOH) was purchased from VWR prolabo (Fontenay-sous-Bois, France); (3) hexamethylenetetramine (hexamine) was supplied by Sigma-Aldrich (Lyon, France); (4) boric acid (purity: 99%) was supplied by Sigma-Aldrich; (5) PMDI resin (by Sigma-Aldrich, purity: 99%).

To prepare adhesive, tannin water solutions were prepared at 40%, 45% and 50% (w/w), to which a 50% (w/w) NaOH solution was added to modify the pH up to 10.0. The solution was gently mixed by mechanical stirrer during the preparation of the glue. Finally to make Tannin/ hexamine glues, 6% hexamine based on the tannins solids content was used as hardener (33% w/w hexamine aqueous solution). The resulting adhesive was mixed for 30 min at room temperature before using. This tannin/hexamine glue was used as a base to formulate other adhesives. 20% PMDI resin was used based on the tannin solids to modify base glue. In the BA containing glues, BA was dissolved in the water before adding tannin. The percentages of BA are based on the tannin solid content. Five different formulations for each tannin concentration were prepared as follows (% additives based on the dry weight of the tannins):

- Tannin/hexamine glue
- Tannin/hexamine glue + 20% PMDI
- Tannin/hexamine glue + 20% PMDI+ 2% BA
- Tannin/hexamine glue + 20% PMDI+ 3% BA
- Tannin/hexamine glue + 20% PMDI+ 4% BA

Before using the glue, solid content (SC %) was measured with three sampling by Equation 2.

$$\text{Equation 2} \qquad SC\% = \left[1 - \left(\frac{m_{\ int} - m_{\ od}}{m_{\ \ int}}\right)\right] \times 100$$

Where $m_{\ int}$ is the initial weight of adhesive and $m_{\ od}$ is the oven dry (at 103 ˚C) weight of glue until constant weight.

These adhesives were used to make 3-ply plywood made of poplar veneers.
Since the grammage used for adhesive (320 g/m^2 for double glue line) and the BA and tannin content in the glues was certain, so the uptake (w/w %) of BA and tannin was calculated based on the oven dry weight (W_{od}) of the plywood samples by simple proportion as Equation 4 using 10 samples with dimension of 50 × 50 mm ^{2} (L × W) × panel thickness. The chemical content in the equations refers to the amount of chemical (g), either BA or tannin, in plywood samples with certain area.

$$Equation\ 3 \qquad Uptake\ \% = \left(\frac{Chemical\ content\ (g)}{W_{od}\ of\ plywood\ samples\ (g)}\right) \times 100$$

Also the retention (kg/m^3) of BA and tannin per cubic meter of plywoods was theoretically calculated based on the grammage of chemicals (kg/m^2). This term is commonly used for solid treated timber. Here to compare the results with other studies, it was calculated based on the approximate number of gluelines in 1m^3 of 6 millimeter thick 3-ply plywoods. It was considered that there are theoretically around 333.2 gluelines (166.6 double gluelines) in each cubic meter of 6 mm thickness 3-ply plywood. The grammage of adhesive applied was 0.32 kg/m^2 (double gluelines), thus by simple proportion the amount of tannin or BA (kg) was calculated based on their concentration in the adhesives for each cubic metre of plywoods.

3.4.1.2 **Mimosa tannin glue**

The main ingredients of the adhesive to make beech plywoods were similar to the quebracho tannin glue which was used for poplar plywood; but the kind of the used tannin was different. The commercial condensed mimosa barks tannin was used to make beech plywoods.
The same guideline, similar to what was mentioned in the previous section, was followed to prepare base tannin/ hexamine glue for gluing beech veneers. The tannins water solution was

prepared at 45% and 50% (w/w) concentration and the resulting base tannin/hexamine adhesives were used to formulate other glues by PMDI and BA addition. It must be point out that BA was added as last ingredient to the glue. In the previous section, BA was dissolved in the water before adding quebracho tannin. Also, Because of positive outcomes of BA addition which was seen in quebracho tannin adhesives; some mimosa tannin adhesives were formulated without PMDI resin. The solution was gently mixed by mechanical stirrer during preparing glue. Five different formulations for each mimosa tannin concentration were prepared as follows (% additives based on the dry weight of the tannins):

- Tannin/hexamine glue
- Tannin/hexamine glue + 5% BA
- Tannin/hexamine glue + 20% PMDI+ 5% BA
- Tannin/hexamine glue + 10% BA
- Tannin/hexamine glue + 20% PMDI+ 10% BA

The resulting adhesives were mixed for 30 min at room temperature before using. Then the solid content of the adhesives was measured with three sampling as Equation 2. These adhesives were used to make 3-ply plywood made of beech. The uptake (%) and retention (kg/m^3) of BA and tannin were calculated in the same manner which was described previously in 3.4.1.1.

3.4.2 Plywoods making with tannin adhesives

The adhesive grammage used was 320 g/m^2 (double line). The adhesive-coated veneer was stacked between two uncoated veneers with the grain directions of two adjacent veneers perpendicular to each other. The stacked veneers were put on a table for 5 min in order to hot press. Press pressure, temperature and duration were applied as 1.2 N/mm^2, 150 ˚C and 6 minutes, respectively. A total of 45 poplar plywoods (450 × 450 × 6 mm^3) and 30 beech plywoods (450 × 450 × 6 mm^3) were prepared corresponding to three panels for each adhesive (Figure 3.2). The pressing machine was different in France and Iran, but same conditions were kept. After hot-pressing, the panels were conditioned at standard climate, before cutting and sampling. The term of standard climate has been used throughout this thesis for conditioning at 20±2 °C; 65±5% relative humidity.

Figure 3.2 Some pieces of beech plywood bonded with tannin adhesive (brown color between veneers shows tannin adhesive)

3.5 Plywoods with treated veneers

In this section, different solutions were made using tannin/hexamine and BA at different concentration to pre-impregnation of veneers prior to pressing and gluing. Then, pre-treated veneers were bonded together with MUF adhesive to make 3-ply plywoods. Since plywood surfaces are usually exposed to environment, so some plywood was made with non-treated core layer to evaluate its effect on durability of the final product. All procedures involving the impregnation and the pressing for beech and poplar veneers were done respectively, in France and Iran.

3.5.1 Treatments and solutions for beech veneers

The main ingredients of the solution for beech veneers include: (1) mimosa tannin; (2) NaOH; (3) hexamine; (4) BA. Suppliers of the chemicals were similar to the materials used to make tannin adhesives.

To prepare solutions, BA was added to deionized water and was stirred at room temperature, to which tannin were added after well dissolving of BA. Before dissolving the tannin, a few drops of NaOH were added in order to dramatically change the pH. The hardener content used was 6% hexamine by weight on tannin extract solids content. The hexamine was dissolved in water to yield a 33% concentration solution before being added to the solution. The solution was mixed and 10% of NaOH (at 50% w/w) based on the tannin solid content was added to modify the pH up to 10.0. The resulting solution was mixed for 30 min at room temperature before using.

Two different concentrations of tannin and BA were formulated to treat beech veneers. The solutions used were 10% tannin + 0.5% BA (Table 3.1) and 20% tannin + 1% BA (Table 3.2). As can be seen from the tables, the final percentage of BA and tannins in the solution were a bit low compared to the formulations. It was due to adding some another chemicals like NaOH and hexamine to the solutions. In the rest of study, the content of tannin and BA in the formulation will be used to describe corresponding solutions.

Table 3.1 Formulation for 10% Tannin + 0.5% BA to treat beech veneers.

Additive For 1.028 kg	Concentration (w/w)	Water g	G total	% In final solution (w/w)
		In 1 kg		
Tannin 100g	92%	8	92	8.9
BA 100g	5%	95	5	0.49
NaOH 10g ca	50%	5	5	0.49
Hexamine 18g	33%	12	6	0.58
Water 800g	100%	800	920	89.5
Total			1028 gr	

Table 3.2 Formulation for 20% Tannin + 1% BA to treat beech veneers.

Additive For 1.028 kg	Concentration (w/w)	Water g In 1 kg	G total In 1 kg	% In final solution (w/w)
Tannin 200g	92%	16	184	18.8%
BA 200g	5%	190	10	0.98%
NaOH 20g ca	50%	10	10	0.98%
Hexamine 36g	33%	24	12	1.16%
Water 572g	100%	572	812	78.08%
Total			1028 gr	

BA standalone solutions were used for comparing results and evaluating the tannin-boron system efficacy. The solutions with 0.49% and 0.98% BA content were used for 0.5% and 1% BA respectively to be as much as BA content in the tannin including formulations. For making BA alone solution, BA and distilled water were stirred mechanically in the plastic beaker until BA became dissolve in the water (without any other ingredients). Throughout this dissertation, 0.5% and 1% BA will be used to refer to 0.49% and 0.98% BA, respectively.

About 25 kg preservative solution was needed based on the impregnation cylinder volume (Figure 3.3). Treatment with distilled water was also considered to compare the results with untreated control samples. The different configurations and treatments for beech veneers are presented in Table 3.3.

Figure 3.3 Impregnation cylinder in the enstib/ Epinal with a capacity of 25 liters

Table 3.3 Configurations of veneers and treatments to make 3-ply beech plywood (-: untreated, + treated)

Beech plywood	Control	Treatment with water	0.5% BA	0.5% BA	10% Tannins + 0.5% BA	10% Tannins + 0.5% BA	1% BA	1% BA	20% Tannins + 1% BA	20% Tannins + 1% BA
Ply 1	-	+	+	+	+	+	+	+	+	+
Ply 2	-	+	+	-	+	-	+	-	+	-
Ply 3	-	+	+	+	+	+	+	+	+	+

3.5.2 Treatments and solutions for poplar veneers

The main ingredients of the solution to treat poplar veneers were similar to the beech veneers; but the kind of the used tannin was different. Quebracho tannin was used to prepare solutions for impregnation of poplar veneers.

The same guideline, similar to what was mentioned in the previous section, was followed to make solution for poplar veneers. One concentration of tannin and BA was formulated to treat poplar veneers. The solution used was 10% tannin + 1% BA (Table 3.4). NaOH and hexamine were added similar to previous section (3.5.1). As can be seen, the BA and tannin content in the solution is lower than formulation. The solution with 0.98% BA content was also prepared for 1% BA solution to be as much as BA content in the tannin including formulation. In the rest of the study, the content of tannin and BA in the formulation will be used to describe corresponds solution, also 1% BA refers to 0.98% BA.

About 25 kg preservative solution was also needed based on the impregnation cylinder volume in Iran. The different configurations and treatments for poplar veneers are presented in Table 3.5. The content of tannin and BA in the solution is lower than formulation (Table 3.5).

Table 3.4 Formulations for 10% tannin + 1% BA to treat poplar veneers.

Additive For 1.028 kg standard formulation	Concentration (w/w)	Water g	G total	% In final solution (w/w)
		In 1 liter		
Tannin 100g	92%	8	92	8.9
BA 100g	5%	95	5	0.98
NaOH 10g ca	50%	5	5	0.49
Hexamine 18g	33%	12	6	0.58
Water 800g	100%	800	920	89.0
Total			1028 gr	

Table 3.5 Configurations of veneers and treatments to make 3-ply poplar plywood (- untreated, + treated)

Poplar plywood	Control	Treatment with water	1% BA	10% tannin + 1% BA	10% tannin + 1% BA
Ply 1	-	+	+	+	+
Ply 2	-	+	+	+	-
Ply 3	-	+	+	+	+

3.5.3 Impregnation process

The veneers were dried in the oven at the 103 °C until constant weight (M_0). They were then placed into the impregnation cylinder and 8 mbar vacuums was applied for 30 minutes to remove

the air trapped in the wood cells. Then cylinder was filled up with the solution and the pressure was slowly increased up to environmental pressure. After two hours, the samples were withdrawn from cylinder and left in the solution for 24 hours. The veneers were weighed after treatment (M_1). The veneers were then placed in a 103°C oven for 24 hours to allow the tannin-hexamine resin to harden. Some sticks were also placed between veneers for event circulation of hot air across the surfaces of the veneer and to providing a more uniform drying rate. After drying, the oven dry weight of veneers (M_2) was measured to calculate the chemical uptake.
The uptake percentage of the preservatives per weight unit and preservative retained per unit volume of wood are calculated by the following equations. When there was just BA in the solution, the percentage of the BA was considered to calculate dry weight of the preservative in the treated veneers.

$$Equation\ 4 \qquad A = M_1 - M_0 \times (\frac{chemical\ content\ in\ preservative\ solution}{100})$$

$$Equation\ 5 \qquad Uptake\ \%\ based\ on\ the\ dry\ weigth = (100\ \times A)/M_2$$

$$Equation\ 6 \qquad kg/m^3 = (A/V) \times 10^3$$

Where,
A: Dry weight of chemical in the uptake solution (g)
M_0: Oven dry weight of the veneers before treatment (g)
M_1: Wet weight of the veneers after treatment (g)
M_2: Oven dry weight of the veneers after treatment (g)
V: Volume of the veneers M^3 in air dried condition

The average retention and uptake of veneers were considered as total retention of plywood when all veneers were treated. But For 3-ply plywoods with non-treated core layer, two-thirds of average retention in the surface veneers was considered as total retention and uptake.

3.5.4 MUF resin

Treated veneers were bonded together with MUF adhesive plus 10% PMDI based on the solid content of MUF to improve adhesive quality against water. Also 10% olive pit powder as filler and 1% chloride ammonium as hardener were added to the glue based on MUF solids. Finally, 300 g of this resin was used to produce 1m^2 3-ply plywood (double glue line). The solid content of MUF resin which was used in France was 61% ± 1 (based on 6 replicates as Equation 2). This resin was produced experimentally in the laboratory (enstib, Epinal). MUF resin that was used in Iran was prepared by Tiran Chime Company which was a mixture of urea-formaldehyde (70% w/w) and melamine-formaldehyde (30% w/w) adhesive. The solid content of this adhesive was 53% ± 1 (based on 6 replicates as Equation 2).

3.5.5 Plywoods making with treated veneers

Treated and non-treated veneers were used to produce plywood after one week conditioning in standard climate (20±2 °C; 65±5% relative humidity). The adhesive grammage was 300g/m^2 (double line). The adhesive-coated veneer was stacked between two uncoated veneers with the grain directions of two adjacent veneers perpendicular to each other (three-ply plywood). The stacked veneers were put on a table at ambient environment for 5 min in order to hot press. Press pressure, temperature and duration were applied as 1.2 N/mm^2, 150 $^\circ$C and 6 minutes, respectively. A total of 44 beech plywoods (450×450×6 mm^3) were prepared corresponding to four panels for each treatment as well as, a total of 15 poplar plywoods (450×450×6 mm^3) were prepared corresponding to three panels for each treatment (Figure 3.4). Before cutting and sampling, plywoods were conditioned at standard climate.

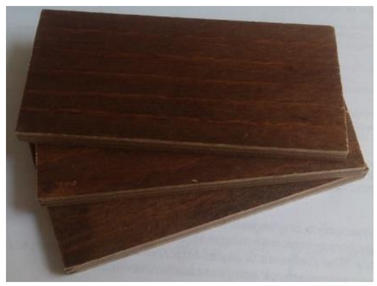


Figure 3.4 Some pieces of beech plywoods made of treated veneers with tannin-boron based solution

3.6 Cutting Pattern of the boards

The panels were cut after conditioning at standard climate for two weeks. About 5 cm from the edges were cut off and discarded. The sampling and cutting patterns of panels as well as more details about each test sample size and its applications are given in Annex A. (Figure A.1 & Table A.1).

CHAPTER 4: Methodology

4.1 Testing on the tannin/hexamine + boric acid adhesive

Thermomechanical analysis, Fourier transform infrared spectroscopy, and matrix-assisted laser desorption/ionization time-of-flight were done on the boron-tannin resin to bring more information about the effect of BA addition on the tannin adhesive features.

4.1.1 Thermomechanical analysis (TMA)

TMA measures the changes in a mechanical property of the sample while it is subjected to a temperature regime. In order to understand how hardening reactions of glue mixes occurs, tannin/ hexamine glue alone and in mixture with PMDI and BA were tested dynamically by a TMA equipment. Also, TMA study was done on the experimental MUF adhesive under influence of adding PMDI resin. Thus, modulus of elasticity (MOE) of the adhesives was studied using a TMA apparatus (Mettler TMA 40, Hightstown, NJ, USA) in three point bending (Figure 4.1). Two beech (*Fagus sylvatica*) wood piles ($21 \times 6 \times 0.55$ mm^3, L × W × T) were bonded to each other with 30 mg of each adhesive. Then, they were tested in non-isothermal mode between 25°C to 250 °C, at a heating rate of 10 °C/min, on a span of 18 mm and exercising a force cycle of 0.1/0.5 N on the specimens with each force cycle of 12 seconds (6 s/6 s). TMA test was repeated at least three times for the each glue on basis of the data dispersion. Finally the maximum of MOE and its increase corresponding to temperature and time were recorded as criteria of glue performance.

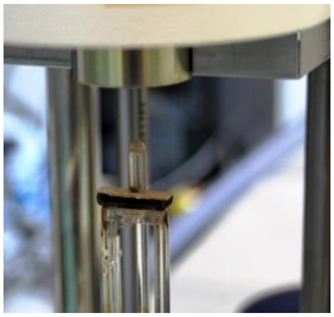


Figure 4.1 TMA apparatus in enstib, Epinal

4.1.2 Fourier transform infrared spectroscopy (FTIR)

FT-IR was used to study the functional groups and structural characteristics of the following tannin adhesives.

- 50% mimosa tannin/hexamine
- 50% mimosa tannin/hexamine + 10% BA

More details about these adhesives are already described (3.4.1.2). The adhesive containing 10% BA was selected due to easier trace of BA function in the glue. FTIR data were collected using a SHIMADZU IRAffinity-1 FTIR spectrophotometer. The tannin adhesives were dried in oven (at 70 ˚C), then 0.2 milligram of dried adhesive were added into potassium bromide (KBr) powder

(30 mg), mixed and grinded to powder which diameter reached 2 micron, then pressed to a small piece sample in a press machine. This sample was placed in the spectrophotometer. The spectrum was obtained in absorbance measurement by combining 32 scans with a resolution of 2.0. The detection of peaks was done by referring to Kim and Kim (2003); Pantoja-Castro and Gonzalez-Rodriguez, (2012); Ping et al. (2012); Puică1 et al. (2006).

4.1.3 Matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF)

MALDI-TOF is tool for the study of polyflavonoid tannin oligomer (Abdalla et al., 2014; Pasch et al., 2001). It was done on following tannin glues:

- 50% mimosa tannin/hexamine
- 50% mimosa tannin/hexamine + 10% BA

More details about these adhesives are already described in 3.4.1.2. Samples for MALDI-TOF analysis were prepared first dissolving 5 mg of sample powder in 1 mL of a 50:50 v/v acetone/water solution. Then 2 µL of this solution is added to 2 µL of a 2,5-dihydroxy benzoic acid matrix. The locations dedicated to the samples on the analysis plaque were first covered with 2 µL of a NaCl solution 0.1 M in 2:1 v/v methanol/water, and predried. Then 1 µL of the sample solution was placed on its dedicated location and the plaque is dried again. MALDI-TOF spectra were obtained using an Axima-Performance mass spectrometer from Shimadzu Biotech (Kratos Analytical Shimadzu Europe Ltd., Manchester, UK). The irradiation source was a pulsed nitrogen laser with 3-ns intervals at a wavelength of 337 nm. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20-kV accelerating voltage), and 100 to 150 pulses per spectrum. The delayed extraction technique was used to apply delay times of 200 to 800 ns. The spectrum precision is of ±1 Da. Each peak value in the resulting positive mode spectrum must be subtracted of 23 Da, this being the molecular weight of the Na^+ included as NaCl in the matrix and attached to the oligomers, to obtain the molecular weight of the chemical species of the peak.

4.2 Testing on the plywood samples

Different physical, mechanical, and biological experiments were carried out on the plywood samples which are described in this section.

4.2.1 Physical properties

Some physical properties were measured such as density, moisture content, swelling and water absorption. Before doing tests, the samples were conditioned at 20°C, 65% RH for at least one month until constant weight.

Constant conditioning weight was considered as having been reached when the results of two successive weighing operations, carried out at an interval of 24 h, do not differ by more than ± 0.05 g. Throughout this dissertation, the term constant conditioning weight refers to this description.

For each type of the panel 10 specimens were used for the evaluation of each physical property. The samples were square with a side length of 50 ± 1 mm and thickness was according to the panel thickness.

4.2.1.1 **Density and moisture content**

The density and the moisture content (MC %) were measured according to EN 323 (1993) and EN 322 (1993) respectively. The conditioning weight and dimensions of the samples were measured by an electrical balance and a digital slide caliper respectively. Then volume of the samples was calculated. The oven dry weight and dimensions of samples were obtained after drying the samples at 103±2 °C until constant weight is reached. Density (D) was determined in both conditioning and oven dry statuses by Equation 7 and 8 respectively. Since conditioning MC at 20°C, 65% RH is approximately equivalent to 12%, so the term of Density at 12% is referred to the conditioning density at 20°C, 65% RH.

$$Equation\ 7 \qquad D_{12\%} = \left(\frac{\mathrm{m}_{con}}{\mathrm{v}_{con}}\right) \times 10^3$$

$$Equation\ 8 \qquad D_{od} = \left(\frac{\mathrm{m}_{od}}{\mathrm{v}_{od}}\right) \times 10^3$$

Where $\mathrm{D}_{12\%}$ is the conditioning density (kg/m^3), $\mathrm{m}_{\mathrm{con}}$ is the conditioning weight (gr), $\mathrm{v}_{\mathrm{con}}$ is the conditioning volume of the plywood sample (mm^3). And where $D_{\ od}$ is the oven dry density (kg/m^3), m_{od} is the oven dry weight (g) and v_{od} is the oven dry volume (mm^3) of the plywood sample.

Conditioning moisture content (MC %) was calculated by Equation 9.

$$Equation\ 9 \qquad MC\% = \frac{m_{\ con} - m_{\ od}}{m_{\ od}} \times 100$$

Where $m_{\ con}$ is the conditioning weight (g) and $m_{\ od}$ is the oven dry weight of the plywood samples until constant weight.

4.2.1.2 **Swelling and water absorption**

The swelling and water absorption were determined according to EN 317 (1993) by measuring the increase in dimensions and weight of the samples after complete immersion in water for 2 and 24 hours. Test pieces were conditioned to constant weight at 20°C, 65% RH. Then, the samples were immersed in clean water, having a pH of 7 ± 1 and a temperature of 20 ± 1 °C. This temperature was maintained throughout the test period. The weight and dimension of the samples were measured by using electrical balance and digital slide caliper respectively. The thickness was measured at the intersection of the diagonals (Figure 4.2).

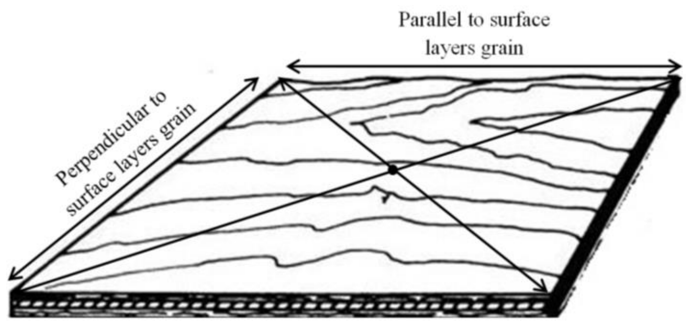


Figure 4.2 Test pieces for the measurement of swelling and water absorption

The water absorption (W.A. %) was calculated by the following equation:

$$Equation\ 10 \qquad W.A.(\%) = \frac{m_2 - m_1}{m_1} \times 100$$

Where m_1 is the weight of the sample before immersion in water and m_2 is the weight of the sample after immersion in water.

The swelling was calculated for the thickness as well as parallel and perpendicular directions to the grain of surface layers using the following equation:

$$Equation\ 11 \qquad D.S.(\%) = \frac{d_2 - d_1}{d_1} \times 100$$

Where d_1 is the dimension before immersion in water and d_2 is the dimension after immersion in water. As the case d can be the thickness or the dimension of the samples either parallel or perpendicular to the grain of surface layers.

4.2.2 Tensile shear strength

Tensile shear tests as bonding quality criterion was carried out according to EN 314-1(2004). The test samples of plywood were prepared as shown in Figure 4.3. Each test sample was cut so that the grain direction of the layer between the gluelines under test was perpendicular to the length of the test piece. The length of samples was 100 mm which was parallel to the grain orientation of surface layers. The width of samples was 25 mm which was perpendicular to the grain orientation of surface layers.

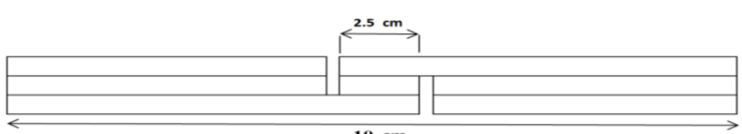


Figure 4.3 Test piece example for a 3 ply veneer plywood

Tensile shear test was done on the samples which were pretreated with different conditions. The choice of pre-treatment was done based on the EN 314-2 (1993) information. Based on this standard, there are different pretreatment for each class of plywood. In this study the plywoods made of tannin adhesive were considered for bond class 1. This bonding class is appropriate for normal interior climate. Two pre-treatments were intended for this bond class before testing shear strength.

1- After conditioning in standard climate (20±2 °C; 65±5% R. H.)
2- After conditioning in standard climate and then immersion for 24 h in water at 20±2°C

The plywood panels made of treated veneers and bonded with MUF adhesive were considered for bond class 2. This class is appropriate for humid conditions or covered exterior. Three pre-treatments were intended for this class.

1- After conditioning in standard climate
2- After conditioning in standard climate and then immersion for 24 h in water at 20±2 °C
3- Immersion for 6 h boiling water followed by cooling in water at 20±2 °C for 1 h

For each set of plywood and pre-treatment, the mean shear strength was measured for 10 test samples. The dimensions of the shear areas were measured by a digital slide caliper before the test for all of the specimens. The tests were determined on an Instron 4467 materials testing machine. The crosshead speed was 1 mm/min. The loading continued until a break of the specimen occurred. The maximum load was recorded, and calculated as shear strength by the following equation:

$$Equation\ 12 \qquad f_v = \frac{F_{max}}{l_1 \times b_1}$$

Where f_v is the tensile shear strength (N/mm^2=MPa), F_{max} is the applied maximum force in Newton (N), l_1 is the length of the shear area in millimeters (mm) and b_1 is the width of the shear area in millimeters

4.2.3 Leaching test

Every wood preservative based on the boron compounds is sensitive to the leaching action of the water. The Leaching test is a method to intentionally expose treated wood to water, in order to measure the amount of emissions.

Commonly used leaching tests for preservative treated wood in Europe are EN 84 (1997) and EN 1250-2 (1995) which were performed on the samples before biological tests.

In the present study, leaching procedure was applied by both leaching tests to assess the efficacy of condensed tannin in fixing of boron.

In this regards 6 samples with dimension of 50 × 50 mm ^{2} (L × W) × panel thickness and 6 samples with dimension of 50 × 25 mm^2 (L × W) × panel thickness were leached according to the two normative methods. Prior to leaching procedure, the samples were conditioned at 20°C, 65% RH. The conditioned weight of samples was taken before start leaching test (m_{con}). The oven dry weight of the samples (m_{od}) was theoretically calculated based on the moisture content (MC %) of humidity controls as the following equation:

$$Equation\ 13 \qquad m_{od} = m_{con} - \left(\frac{(m_{con} \times MC\%)}{100}\right)$$

The MC % of humidity controls were calculated as Equation 9.

4.2.3.1 **EN 84**

This European standard specifies a leaching procedure applicable to wood samples that have been treated previously with a preservative in order to evaluate any loss in effectiveness when the test samples are subjected subsequently to biological tests compared with samples which have not undergone any leaching procedure. EN 84 is stricter and intense compared to EN 1250-2. For the leaching, samples were covered with deionized water in an amount of five times the volume of the sample (1 volume plywoods to 5 volume of water). The impregnation vessel was then held in 4 kPa of vacuum for 20 min. After vacuum, the samples stayed in the water for 2 h before the water was changed for the first time. Specimens were submersed in deionized water (water grade 3 according to ISO 3696 (1995)) for 14 days. There was no water stirring during leaching. Water was exchanged nine times in 14 subsequent days. Water replacement is mandatory first and second days. The remaining seven times carried out in 12 remaining days at intervals of minimum 1 day and maximum 3 days. During the test, the samples were separated from each other and from the bottom and sides of the water vessel (Figure 4.4). After each water replacement around 20 ml leachate water was collected and retained for the chemical analysis. After leaching procedure, the specimens were conditioned until constant weight at 20°C, 65% RH. Once the samples were conditioned, anhydrous weight of the samples (dried at 103 $^{\circ}$C) was recorded. The color changes of water and delamination of plywood samples were recorded during the experiments.

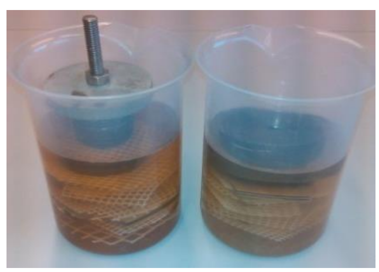


Figure 4.4 Samples during leaching procedure based on the EN 84 (1997)

4.2.3.2 **EN 1250-2**

EN 1250-2 leaching test is a more dynamic method in which the treated samples are immersed in constantly stirred water with a magnetic stirrer. This leaching test requires the shorter leaching time compared with EN 84; it is completed in only four days. Some grid was used for making water circulation using magnet stirrer as shown in Figure 4.5 (left). The samples were covered with 500 and 1000 ml deionized water according to the two sample dimensions (500 ml for 6 samples with dimensions of 50 × 25 mm^2 (L × W) × panel thickness and 1000 ml for 6 samples with dimensions of 50 × 50 mm^2 (L × W) × panel thickness). Water circulation rate was determined based on the vortex height in the centre of the vessel. It was adjusted to make vortex as big as half of the water height (Figure 4.5; centre).

Figure 4.5 Left: holder made by plastic grid to keep samples; Centre: the height of vortex in the test vessel; Right: the test vessel on the magnet stirrer

This leaching test has 6 periods comprising 1, 2, 4, 8, 16 and 48 hours. After each period the leachate was collected and replace with fresh water. Between the third and fourth period the samples were left in the test vessel without water for 16 hours. After leaching procedure, the specimens were conditioned for minimum two weeks at 20°C, 65% RH. Once the samples were conditioned, anhydrous weight of the samples (dried at 103 °C) was recorded prior to biological tests.

4.2.4 Biological test

Fungal and termite tests have been done with and without leaching on the samples.

4.2.4.1 **Fungal test**

Fungal test has been done according to ENV 12038 (2003). Three plywood samples with dimension of 50 × 50 mm ^{2} (L × W) × panel thickness were used for each treatment.

Virulence control was performed on 6 untreated *Populus deltoides* as well as *Fagus sylvatica* solid woods with standard dimensions of 50 × 25 × 15 mm^3 (Length × Radial × Tangential). Also, three blocks from *Populus deltoids* and *Fagus sylvatica* with the same dimensions as the plywood specimens 50 × 50 × 6 mm^3 (L × R × T) were exposed to fungi as control samples. The samples were exposed to fungal attack against *Trametes versicolor* (strain: CTB 863A; white rot) grown on malt/agar medium (malt 40g/l, agar 20g/l).

Initial oven dry weight (m_1) of the plywood samples was theoretically obtained according to Equation 13 by humidity controls. Massive wood blocks were oven dried at 103°C to have their initial weight (m_1).

All plywood specimens were sterilized by gamma radiations prior to fungal exposure. In each culture flask, one treated specimen was introduced. The flask was provided with leak-proof lids, the centre of which was pierced with a round hole of up to 15 mm diameter and blocked with compressed cotton so as to allow ventilation but to prevent access by contaminating fungi (Figure 4.6). The samples were incubated for 16 weeks at 22°C, 70% RH. After this, the mycelium was removed and the specimens were weighted (m_2) to determine their moisture content (MC %) at the end of the fungal exposure by Equation 14.

$$Equation\ 14 \qquad MC\ \%\ at\ the\ end\ of\ the\ test\ = \frac{m_2 - m_1}{m_{\ 1}} \times 100$$

Where $m_{\ 1}$ is the oven dry weight and $m_{\ 2}$ is the weight of the samples at the end of the test.

The specimens were then dried at 103 °C and their final weight (m_3) was recorded. Then, weight losses (WL %) were determined as a percentage of the initial weight by Equation 15. The weight loss was used as the criterion for determining the extent of attack.

$$Equation\ 15 \qquad WL\,\% = \frac{m_1 - m_3}{m_1} \times 100$$

Figure 4.6 Culture flasks that one sample was introduced in each one on the stainless steel supports

4.2.4.2 **Termite Test**

The exiting standard references for efficacy tests against termites are EN 118 (2014) and EN117 (2013). Another adapted choice test was also designed to carry on plywood samples based on the EN 117. All termite tests were done before and after leaching process to find out tannin-boron efficacy.

Termites of the species *Reticulitermes flavipes* (*ex. santonensis*) were collected on Oleron Island (France) and transported to the laboratory (Figure 4.7). In laboratory, termites were extracted by gently opening and bating wood logs and stakes, and then they were separated from the residues of wood (Figure 4.8; left). Termites were placed in breeding boxes for six months at 27 ± 2 °C and 75 ± 5 % R.H. until their extraction before tests (Figure 4.8; right). During this period termites were fed by poplar wood.

Prior to exposure, the conditioned moisture content was calculated in a series of samples from each panel type to determine the dry weight of the main samples prior to exposure (as Equation 13 for fungal test). The normative methods for termite test will be described below.

Figure 4.7 Right: collecting termites on Oleron Island (France); Left: transporting them to the laboratory (Cirad, Montpellier)

Figure 4.8 Right: termites extracted from infested wood; Left: breeding boxes in conditioning room

4.2.4.2.1 **EN 117**

This standard specifies a method for the determination of the toxic values of a wood preservative against the *Reticulitermes* species of European termites. In this method termites can be in contact with all sides of the specimens.

The nominal dimension of each test sample was 50 × 25 mm^2 (L×W) × panel thickness by using 3 replicates per treatment. For each termite colony and set of the test, reference control was performed on 3 untreated Scots pine (*Pinus sylvestris*) solid sapwood with standard dimensions (50 × 25 × 15 mm^3; L × R × T). Additional tests were also carried out using 3 untreated poplar (*Populus deltoides*) as well as beech (*Fagus sylvatica*) solid woods with standard dimensions (50 × 25 × 15 mm^3; L × R × T). Also, three blocks from *Populus deltoids* and *Fagus sylvatica* with the same dimensions as the plywood specimens (50 × 50 × 6 mm^3; L × R × T) were exposed to termite attack.

The substrate for establishing the colonies was Fontainebleau sand. In a separate container, the sand was remoistened for the test by introducing first the water and then the sand in the proportions of one volume of water to four volumes of sand. Then, in each test container was formed a layer of remoistened, non-compacted sand 40 mm – 50 mm thick. Some holes (3-4) were left in the sand, in order to let the termites move inside and air circulate. Small pieces of the original wood (approximately 0.5 g) were placed in the bottom of the container. A Glass rings were placed against one of the vertical walls of the test container and in the middle of this wall; it was placed in the substrate so that it just protrudes the surface. A group of 250 workers from same colony and a number of soldiers and nymphs corresponding to the proportion in the colony (1 % to 5 %) were carefully distributed over the entire substrate. Over a period of one day after setting up the colonies test sample was placed on the glass rings so that it did not touch the substrate surface. The side resting on the ring was one of the narrow longitudinal sides, with a wide longitudinal side in contact with the wall of the test container (Figure 4.9).

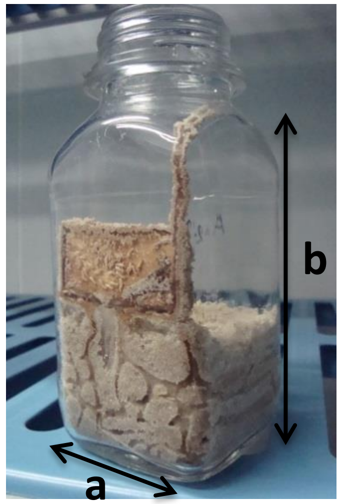


Figure 4.9 A sample of EN 117 non-choice test (a: 7 cm, b: 13 cm)

The test containers were kept in the dark climate cell (27±2 °C and 75±5 % R.H.) for eight weeks. Throughout the duration of the test, the test container was inspected at regular intervals (once a week). The results of the inspections were recorded on a special sheet; and some necessary actions were taken such as prevent termites escape and retain substrate moisture. At the end of the test, the samples were removed from the container and they were carefully cleaned from all particles of substrate and other adhering to their face. The total numbers of worker termites which are still living (n_s) in the container were counted to calculate the survival level of the worker. Also, the presence of living soldiers and nymphs and the number of them were recorded. The survival rate was calculated as Equation 16.

$$Equation\ 16 \qquad Survival\ rate\ \% = \left(\frac{n_s}{250}\right) \times 100$$

The samples were examined and visually rated using EN 117 (2013) guidelines (Annex B). The visual rating and survival rate are only criteria which are described by EN 117. In addition in this study, the weight loss of the samples was determined after exposure to the termites attack. The specimens were dried at 103°C (until constant weight) and their final oven dry weight was recorded. Then, weight losses (WL %) were determined as a percentage of the initial oven dry weight in the same manner as Equation 15 for fungal test.

4.2.4.2.2 **EN118**

This standard specifies a method for the determination of the preventive action of a wood preservative against the *Reticulitermes* species of European termites when the preservative is applied as a surface treatment to wood. The nominal dimension of each test sample was 50 × 50 mm^2 (L×W) × panel thickness by using 3 replicates for each treatment. For each termite colony and set of the test, reference control was performed on 3 untreated Scots pine (*Pinus sylvestris*) solid sapwood with standard dimensions (50 × 50 × 10 mm^3; L × R × T). The controls were three solid blocks from poplar (*Populus deltoides*) and beech (*Fagus sylvatica*) with the same dimensions as the plywood specimens (50 × 25 × 6 mm^3; L × R × T).

According to this method, termites are only in contact with one side of the test specimen. In this test one glass tube are attached at the centre of the surface of each sample. The ground glass end of glass tube (110mm length – 25mm width) was attached with colophony resin at the centre of the each specimen. This resin cannot be attacked by the termites and is non-toxic, for securing tube.

An insert was introduced into the each tube and it was placed on the surface of the test specimen (Figure 4.10; right). The inserts are discs of untreated Scots pine (*Pinus sylvestris*) sapwood, 1 mm thick and having a diameter about 1mm to 2 mm less than the interior diameter of the tubes, so that they fit snugly into the tube after moistening. The substrate for establishing the colonies was Fontainebleau sand. In a separate container, the sand was remoistened for the test by introducing first the water and then the sand in the proportions of one volume of water to four volumes of sand. The tubes were filled in about two-third of their volume with remoistened sand which was not pressed down. Two holes were made along the central axis of each tube and some wood from original culture (approximately 0.5 g) were buried in them. A group of 250 workers from same colony and a number of soldiers and nymphs corresponding to the proportion in the colony (1 % to 5 %) were carefully distributed into the tube. The termites which are moulting also those which appear to be wounded and motionless were rejected. The opening side of the tubes was covered with a piece of aluminum foil to prevent evaporation of water and escape of termites. Then, the test assemblies were placed on individual trays to prevent any escape of termite and they were kept in the dark climate cell (27±2 °C and 75±5 % R.H.) for eight weeks (Figure 4.10; left). Throughout the duration of the test, the test assemblies were inspected at regular intervals (once a week). The results of the inspections were recorded on a special sheet; and some necessary actions were taken such as prevent termites escape and re-moistening sand substrate.

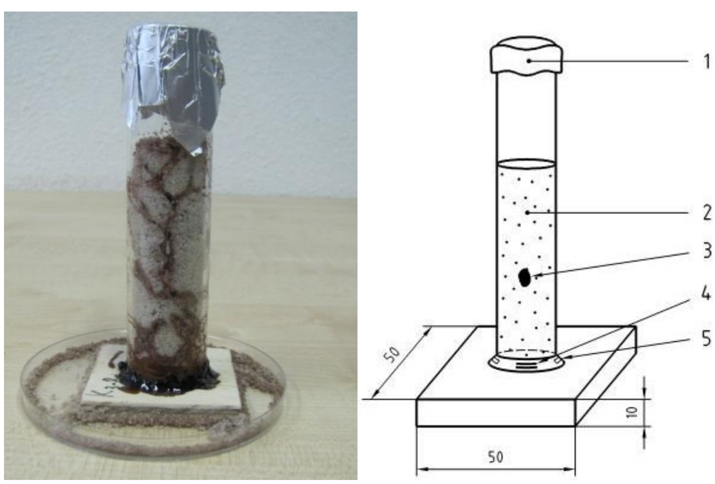


Figure 4.10 Left: a sample of EN 118 non-choice test, Right: schematic diagram of the test assembly for EN 118 (1: capping; 2: substrate; 3: wood from original culture; 4: insert; 5: adhesive)

At the end of the test, the tubes were removed from the samples. The extent of damage to the insert was assessed. Then, the number of live termite workers, soldiers and nymphs were counted in order to determine the worker survival rate (as Equation 16). After cleaning the test samples,

they were classified and visually rated by any evidence of attack, its extent and its depth, in accordance to the EN 118 (2014) guideline (Annex B.).
The weight loss can't be measured for EN 118. This was due to the co-effect of colophony resin which was used to joined glass tube to the test samples.

4.2.4.2.3 **Choice termite test**

Since boron compounds are non-repellent, the choice feeding test could be interesting in present study. So, this method was designed based on the EN 117 method with same standard conditions. But three samples were introduced into the each container at the same time: one untreated samples and two treated ones with different concentrations (Figure 4.11). The dimension of each test sample, the number of termites, and the time of test were similar to EN 117 guidelines. For control test, three untreated plywood samples were placed in the container.
For each set of plywood and termite colony, virulence control was performed on 3 untreated Scots pine (*Pinus sylvestris*) solid sapwood with standard dimensions ($50 \times 25 \times 15$ mm^3; L × R × T). Additional tests also were carried out using 3 samples of Scote pine in each container with three replications. For control test, three untreated plywood samples were placed into each container and repeated three times.
At the end of the test, the samples were removed from the container and visually rated using EN 117 (2013) guideline (Annex B.). The number of live termite workers, soldiers and nymphs were also counted in order to determine the worker survival rate (as Equation 16). Also, the weight loss of samples was determined as Equation 14.

Figure 4.11 Choice feeding test set up with three samples in one container

4.3 Statistical analysis

Data analysis and calculation as well as graphs drawing were done using Excel 2010. The obtained data from different features (biological, physical and mechanical) were analyzed according to the various treatments. The standard deviation (SD), median, and minimum and maximum values of data were used to show the distribution of the data around the mean value. In the next step, analysis of variance (ANOVA) and Duncan multiple range tests were conducted by means statistical program SPSS v15 for different parameters in each set of plywoods between mean values. ANOVA was initially used to identify significant difference between treatments. Based on the results from ANOVA, the grouping was done by Duncan tests.

CHAPTER 5: Retention and characterization of glueline

This chapter presents the results of retention and uptake for both treatments (glue line and veneer), as well as the investigation on tannin/hexamine glue added with boric acid (BA).

5.4 Retention and uptake in plywoods

5.4.1 Glue line treated plywood

In this section, solid content of the adhesives as well as retention and uptake of BA and tannin are separately reported for beech and poplar plywoods made of tannin adhesives.

5.4.1.1 **Poplar plywood**

Table 5.1 shows the solid content of each adhesive, as well as uptake (% w/w) and retention (kg/m^3) of BA and tannin in the poplar plywoods. Solid content (SC %) of the adhesives were strongly depended to tannin concentration and PMDI addition. BA addition did not markedly change solid content. Since the amount of BA was added based on the dry weight of the tannin, increase in the initial concentration of tannin caused increase in BA uptake and retention. The uptake and retention of tannin showed significant reduction following the addition of PMDI, but the addition of BA caused a slight decrease.

The amount of BA loading by glue line treatment for poplar plywood at 4% BA is approximately as much as toxic threshold data reported by Drysdale (1994) to provide protection against Basidiomycetes fungi as well as wood borer beetles (0.8 kg/m^3; 0.16% BAE (w/w)). For ease of comparison, boron compounds are often compared based on the “Boric Acid Equivalent” (BAE) which obviously is the amount of BA that could be formed from the subject compound.

The amount of BA in the gluelines seems to be not enough against termites attack. Commercial retentions recommended for protection against termites are usually in excess of 1% BAE equal to 4.5 kg/m^3 depending on timber density (Schoeman & Lloyd, 1998). But Ahmed et al. (2004) indicated that borate was toxic to termites even at 0.24% w/w BAE and caused significant termite mortality in laboratory experiments (not full protection). It should be taken into account that data reported here in the literatures are related to the solid wood and obtained by pressure or non-pressure treatments. In the case of plywoods with treated glue line, BA has to move through the glueline to protect the plywood. So the effect of BA retention on the durability can be quite different when it is used in the glueline. In the solid wood, the distribution of boron and its mobility throughout the wood is different.

This has been discussed before in the literature reviews (2.6.2) that tannin network conserves sufficient mobility to maintain BA preservative action. Indeed, the efficacy of boron against insects and fungi is linked to its mobility. Any system which is suggested to reduce leaching of boron should retain limited mobility to maintain biocide action of borates (Pizzi & Baecker, 1996).

Table 5.1 Solid content of the adhesives, as well as uptake and retention of BA and tannin in poplar plywoods with treated glueline

	Formulations	SC (Std. dev.) %	BA uptake based on m od (Std. dev.) %	kg BA/m^3 in 3-ply plywoods kg/m3	Tannin uptake based on m od (Std. dev.) %	kg Tannin/m^3 in 3-ply plywoods kg/m3
Tannin 40 %	Tannin/Hexamine	38.02 (1.03)	0	0	1.46 (0.06)	18.54
	Tannin/Hexamine + PMDI	40.10 (0.92)	0	0	1.40 (0.14)	17.31
	Tannin/Hexamine + PMDI + BA 2%	40.12 (0.87)	0.082 (0.006)	0.343	1.35 (0.10)	17.19
	Tannin/Hexamine + PMDI + BA 2%	40.63 (1.02)	0.125 (0.008)	0.513	1.33 (0.08)	17.14
	Tannin/Hexamine + PMDI + BA 2%	40.85 (0.53)	0.191 (0.012)	0.684	1.29 (0.09)	17.09
Tannin 45 %	Tannin/Hexamine	42.23 (0.47)	0	0	1.59 (0.06)	20.48
	Tannin/Hexamine + PMDI	44.12 (0.93)	0	0	1.46 (0.08)	19.02
	Tannin/Hexamine + PMDI + BA 2%	44.55 (0.84)	0.109 (0.008)	0.373	1.47 (0.14)	18.89
	Tannin/Hexamine + PMDI + BA 3%	44.54 (0.39)	0.153 (0.012)	0.560	1.50 (0.13)	18.82
	Tannin/Hexamine + PMDI + BA 4%	44.96 (0.63)	0.197 (0.014)	0.746	1.48 (0.10)	18.76
Tannin 50 %	Tannin/Hexamine	46.51 (0.71)	0	0	1.83 (0.15)	22.40
	Tannin/Hexamine + PMDI	49.88 (0.89)	0	0	1.69 (0.09)	20.66
	Tannin/Hexamine + PMDI + BA 2%	50.01 (0.46)	0.105 (0.013)	0.377	1.64 (0.21)	20.50
	Tannin/Hexamine + PMDI + BA 3%	50.00 (0.37)	0.155 (0.016)	0.607	1.63 (0.17)	20.42
	Tannin/Hexamine + PMDI + BA 4%	50.3 (0.57)	0.200 (0.017)	0.811	1.57 (0.15)	20.34

SC%: Solid content of the adhesive; m_{od}: Oven dry weight of the plywood samples

5.4.1.2 **beech plywood**

The solid content of each adhesive, as well as uptake and retention of BA and tannin in the beech plywoods are given in Table 5.2. The results for beech plywood were similar to those obtained for poplar plywood. The solid content of the adhesives were strongly depended to the initial concentration of the tannins and the addition of PMDI. The addition of PMDI reduced BA and tannin concentration in the glues and consequently decreased their retention in the plywoods.

The uptake of BA at 5% is lower than those obtained at 4% for poplar plywood in the same tannin concentration. It is due to lower density of the poplar wood than the beech. The amount of BA loading at 5% seems to be enough to make protection against fungal attack. But even at 10% BA, still the amount of loading is less than values reported in literatures for solid wood to provide full protection against termites. The maximum loading was occurred at 50% tannin+

10% BA which was 0.364 % (w/w) and 2.150 kg/m^3, whereas generally around 1.0% w/w BAE (base on wood dry weight) is necessary to provide protective effect against termites attack (Drysdale, 1994; Lloyd, 1998). On the other hand, BA was loaded in the gluelines which can cause different mobility and efficacy for boron against biological attack.

Our experimental observation showed that the additional loading of BA is not possible into the tannin glue. Even with 10% BA, adhesive became very gelatinous and hard after a few minutes in the room temperature. The applying of adhesive on the surface of veneers was difficult with 10% BA in the glue. Further studies on the thermomechanical and mechanical properties showed more negative effects of loading 10% BA into the tannin glue (5.5.3.2).

Table 5.2 Solid content of the adhesives, as well as uptake and retention of BA and tannin in beech plywoods with treated glueline

	Formulations	SC (Std. dev.) %	BA uptake based on m od (Std. dev.) %	kg BA/m^3 in 3-ply plywoods kg/m3	Tannin uptake based on m od (Std. dev.) %	kg Tannin/m^3 in 3-ply plywoods kg/m3
Tannin 45 %	Tannin/Hexamine	41.04 (0.10)	0	0	1.06 (0.04)	20.48
	Tannin/Hexamine + BA 5%	41.97 (0.21)	0.167 (0.004)	1.005	1.05 (0.03)	20.10
	Tannin/Hexamine + PMDI + BA 5%	43.15 (0.26)	0.143 (0.005)	0.934	0.99 (0.04)	18.69
	Tannin/Hexamine + BA 10%	42.24 (0.33)	0.330 (0.006)	1.973	1.03 (0.02)	19.73
	Tannin/Hexamine + PMDI + BA 10%	43.97 (0.23)	0.321 (0.013)	1.837	1.01 (0.04)	18.37
Tannin 50 %	Tannin/Hexamine	45.87 (0.31)	0	0	1.15 (0.03)	22.40
	Tannin/Hexamine + BA 5%	46.02 (0.49)	0.182 (0.005)	1.097	1.14 (0.03)	21.94
	Tannin/Hexamine + PMDI + BA 5%	48.22 (0.42)	0.175 (0.001)	1.013	1.10 (0.02)	20.27
	Tannin/Hexamine + BA 10%	46.64 (0.87)	0.364 (0.010)	2.150	1.14 (0.03)	21.50
	Tannin/Hexamine + PMDI + BA 10%	49.09 (0.65)	0.325 (0.008)	1.989	1.02 (0.03)	19.89

SC%: Solid content of the adhesive; m_{od}: Oven dry weight of the plywood samples

5.4.2 Plywood made of treated veneers

The retention (kg/m^3) and uptake (w/w) of BA and tannin in the plywoods made of treated veneers are separately given for poplar and beech veneers.

5.4.2.1 **Beech plywood**

Table 5.3 summarized retention and uptake of BA and tannin for beech plywoods. At first glance, it is obvious that retention and uptake of BA and tannin are more than their loading by glue line treatment approach.

Despite the same concentration of BA, its retention was decreased when tannin was present in the solution. It was due to the decrease in the solution viscosity because of tannin present and consequently decreases in the solution uptake. In the solution with 20% tannin, the retention of BA showed 6.49 % reduction compared to the BA alone solution with same BA content.

In the tannin-boron based solutions, the sum of retention or uptake for BA and tannin is less than total taken up. It is because of other material in the solution (hexamine mainly and sodium hydroxide).

The amounts of BA in beech plywoods at 0.5% BA concentration are comparable with data reported in the literatures (Drysdale 1994; Schoeman and Lloyd 1998) to make full protection against fungal attack and wood borer beetles but still not enough against termites. At 1% BA concentration, the amounts of BA loading is as much as minimum toxic threshold suggested in the literatures (Tsunoda, 2001) for the solid wood and WBC to be fully protect against termites damage.

Table 5.3 Retention and uptake of tannin and BA in beech plywoods made with treated veneers

Tannin solution	BA	Core layer	BA		Tannin		Total	
%	%	+ treated -untreated	Retention kg/m^3	Uptake % w/w	Retention kg/m^3	Uptake % w/w	Retention kg/m^3	Uptake % w/w
Control plywood			0	0	0	0	0	0
Treated with water			0	0	0	0	0	0
−	0.5	+	3.17 (0.10)	0.56 (0.03)	0	0	3.17 (0.10)	0.56 (0.03)
−	0.5	−	2.11	0.37	0	0	2.11	0.37
10	0.5	+	2.78 (0.23)	0.43 (0.03)	50.58 (4.21)	7.75 (0.57)	56.66 (4.71)	8.68 (0.64)
10	0.5	−	1.85	0.29	33.72	5.17	37.77	5.76
−	1	+	6.02 (0.34)	1.01 (0.07)	0	0	6.02 (0.34)	1.01 (0.07)
−	1	−	4.01	0.67	0	0	4.01	0.67
20	1	+	5.63 (1.13)	0.80 (0.13)	108.60 (21.81)	15.41 (2.54)	120.31 (24.16)	17.07 (2.82)
20	1	−	3.75	0.53	72.40	10.27	80.21	11.38

5.4.2.2 **Poplar plywood**

The retention and uptake for BA and tannin are reported for poplar plywood in Table 5.4. The uptake and retention of BA in the solution with 1% BA alone was a few lower than those obtained for beech plywoods. It was not expected due to the poplar lower wood density and higher porosity compared to the beech. The explanation is difficult about this case; impregnation process was done in two different laboratories. Similarly to the beech plywoods, despite the same concentration of BA, its retention was decreased when tannin was present in the solution. The retention and uptake of BA for poplar plywoods made with treated veneers are in the range of reported data to make full protection against both fungal and subterranean termites attack (Drysdale, 1994; Lloyd et al., 1998).

Table 5.4 Retention and uptake of tannin and BA in poplar plywoods made with treated veneers.

Tannin solution	BA	Core layer	BA		Tannin		Total	
%	%	+ treated -untreated	Retention kg/m^3	Uptake % w/w	Retention kg/m^3	Uptake % w/w	Retention kg/m^3	Uptake % w/w
Control plywood			0	0	0	0	0	0
Treated with water			0	0	0	0	0	0
−	1	+	5.46 (0.44)	1.68 (0.41)	0	0	5.46 (0.44)	1.68 (0.41)
10	1	+	4.00 (0.20)	0.95 (0.05)	36.37 (1.85)	8.65 (0.43)	42.74 (2.18)	10.17 (0.50)
10	1	−	2.67	0.63	24.25	5.78	28.49	6.78

5.4.3 Conclusions for the results of uptake and retention

1. The uptake and retention values obtained by glue line treatment for beech and poplar plywoods were as much as toxic threshold data reported in literature for solid wood to provide protection against Basidiomycetes fungi as well as wood borer beetle.
2. In the plywoods made of treated veneers the amount of BA loading was more than plywoods with the treated glueline. The uptake and retention of BA at 1% solutions (with or without tannin) was as much as the minimum toxic threshold for the solid wood and WBC to be fully protect against termite damage and also Basidiomycetes fungi.

5.5 Tannin-boron resin characterization

5.5.1 FTIR

FTIR spectroscopy is useful equipment for finding out what kinds of bonds are present in a molecule. The FTIR spectra of 50% mimosa tannin/hexamine (50% Tan.) and 50% mimosa tannin/hexamine + 10% boric acid (50% Tan.+ 10% BA) are shown in Figures 5.1 and 5.2, respectively. The assignments for each spectrum are summarized in Table 5.5.

The spectra of both formulations show a broad absorption band between 3700 and 3000 cm^{-1} which is due to the presence of hydroxyl groups with a maximum at 3313 cm^{-1} for 50% Tan. and at 3385 cm^{-1} for 50% Tan.+ 10% BA, respectively. The bands at 2933 cm−1 and 2712 cm−1 for 50% Tan. at 2928 cm−1 and 2692 cm−1 for 50% Tan.+ 10% BA were due to -C-H- stretching vibration assigned to methyl (CH2) and methylene (CH3) groups respectively. The weak signals at 1695 cm^{-1} for 50% Tan. and 1704 are assigned to carbonyl groups (C=O). The peaks pronounced at 1610-1445 cm^{-1} shows presence of aromatic rings. The signal at 1613 cm^{-1} is characteristic of the elongation of the aromatic double bond (C-C) of the benzene nucleus which was presented in same wavelength for both formulations.

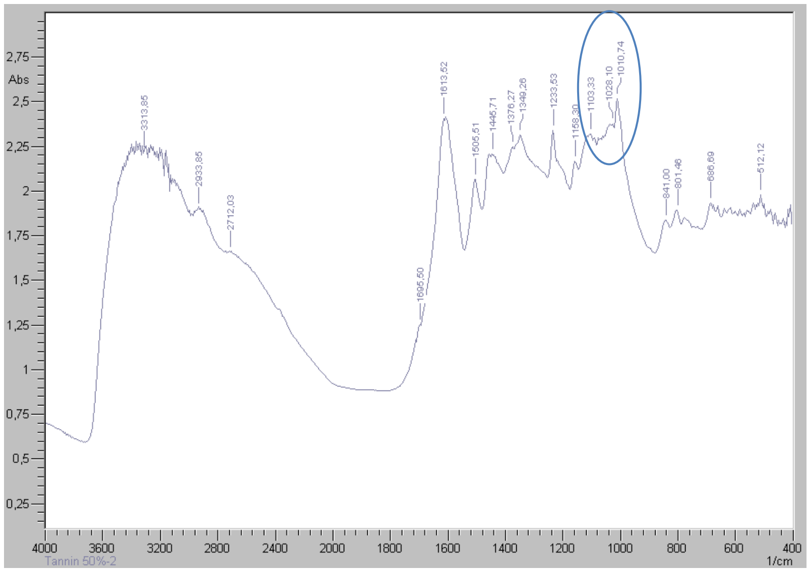


Figure 5.1 FTIR Spectra of 50% tannin/hexamine

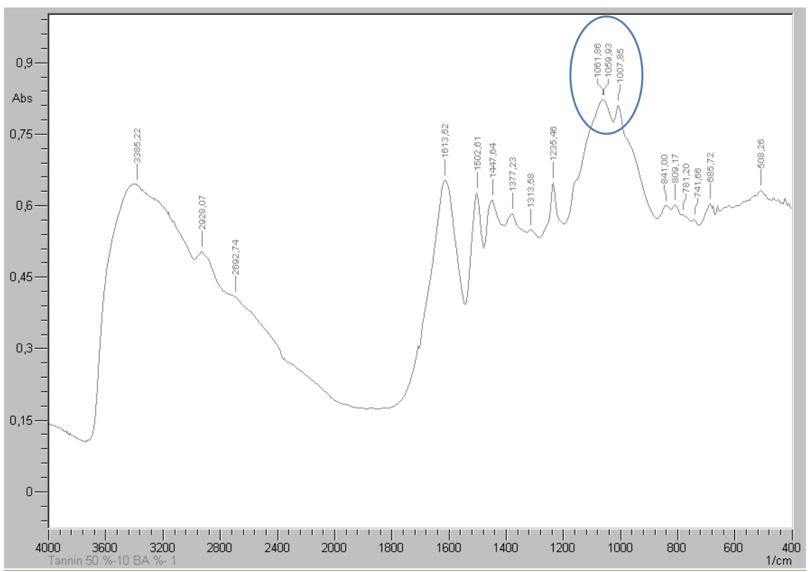


Figure 5.2 FTIR Spectra of 50% tannin/hexamine +10% BA

Table 5.5 Assignment of FTIR spectra of mimosa tannin/hexamine resin with or without BA

Peak (cm^{-1})		Assignment
50% tannin/hexamine	50% tannin/hexamine +10% BA	
3313	3385	-OH stretching vibration
2933, 2712	2928, 2692	-CH3, -CH2 stretching vibration
1695	1704	C=O stretching vibration
1613,1505, 1447, 1235	1613, 1502, 1447, 1233	C-C aromatic squeal vibration
1103,1028, 1010	1061, 1059, 1007	Aromatic carbons linked to -OH groups on the B-ring of the flavonoids
841, 801, 686, 512	841, 809, 685, 508	C-H bond in the benzene rings out of plane bending vibration

The region of peaks 1500-950 cm^{-1} are called fingerprint region for FTIR spectra of tannins, refers to C–O and C–C stretching modes. The absorbance/the peaks were partly the same for 50% Tan. and 50% Tan.+ 10% BA between 1500-1150 cm^{-1}, but with a slight shift and reduction in intensity for BA containing adhesive. These peaks are related to C-C aromatic squeal vibration.

The highest differences between the two formulas are specified with the enclosed areas on the spectra (Figures 5.1 and 5.2). These bands are related to the aromatic carbons which are linked to -OH groups on the B-ring of the flavonoids. These bands became very sharp and strong by BA addition. BA is well known to form orthodiphenol complexes (Di et al. 2011; McClary and Taylor, 2013) with the vicinal -OHs of the B-ring of the flavonoid and this changes the patterns of peaks in that region. Figure 5.3 indicates the changes in a schematic manner by BA addition in this region.

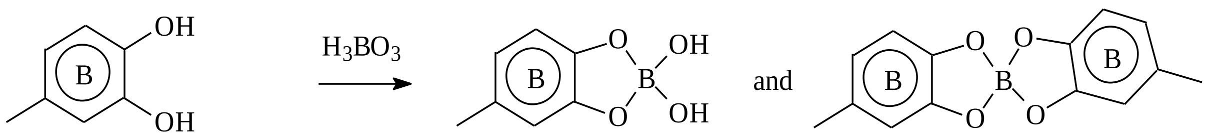


Figure 5.3 Boric acid interactions with vicinal –OHs

The peaks around 910-740 cm^{-1} in spectra are deformation vibrations of the C-H bond in the benzene rings.

5.5.2 MALDI-TOF of mimosa tannin resin with or without boric acid

The major components of flavonoid tannins are building units described in Figure 5.4 with the corresponding molecular weight (Mw). The tannin extracts are primarily composed of these repeating units and smaller fractions of polysaccharides and simple sugars (Pizzi 1994). The major building unit of mimosa tannin is prorobinetinidin (Thébault et al., 2015) with proportion of other units (Pasch et al., 2001).

Figure 5.5 shows MALDI-TOF analysis of mimosa tannin/hexamine resin with the molecular weight ranging from 300 to 450 Da (Figure 5.5 a) and from 450 to 1200 Da (Figure 5.5 b). The peaks of these flavonoid units and their possible combinations to form oligomers on MALDI spectra can be calculate based on the Mw. For example the peak of prorobinetinidin in MALDI spectra is calculated according to: Mw of unit+ Mw of Na^+ + Mw of two H end groups + Mw prorobinetinidin = 23.0(Na) + 2.0 (end groups, 2 × H) + 288.3 (prorobinetinidin) = 313.3 Da. This peak is clear in the Figure 5.5a at 313.66. It should take into account that prorobinetinidin monomer or oligomer formed of this unit gives same peak as like procyanidin (catechin), because both of these units have same Mw.

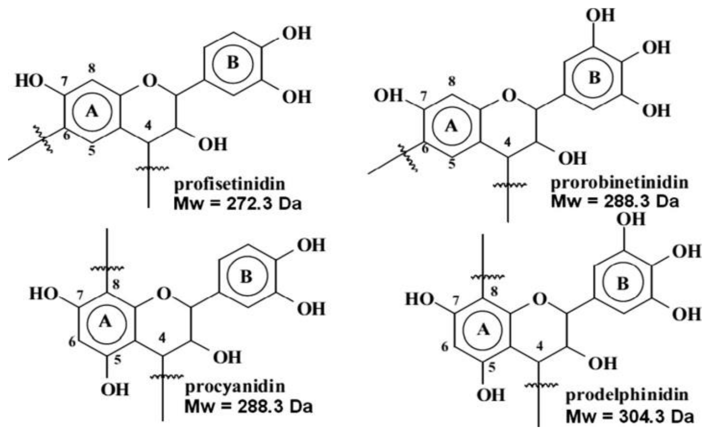


Figure 5.4 The four main structures of flavonoid tannins

The flavonoid units also can be combined together to form dimer, trimer, and or other oligomers. For example, the peak at 569 Da is fisetinidin dimer according to: Mw of Na^+ + Mw of two H end groups + Mw of profisetinidin (×2) = 23.0(Na) + 2.0 (2 × 1) + 544.6 (2 × 272.3) = 569.6 Da. The interpretation of the MALDI spectra for mimosa tannin/hexamine resin in Figure 5.5 yielded the series of oligomer structures which is shown in Table 5.6 with calculated and experimental Da for each structure. The difference between calculated and experimental Da is related to the systematic instrumental error. In this study oligomers with a molecular weight lower than 1200 Da were studied. Note that the predominant repeat unit in this tannin is 288 Da, indicating that this tannin is predominately a prorobinetinidin (Pasch et al., 2001).

Table 5.6 MALDI-TOF fragmentation peaks for mimosa tannin/hexamine

Oligomer or monomer + Na^+ + 2 H	Flavonoid unit types				Calculated Mw (Da)	Experimental Mw (Da)
	prorobinetinidin	profisetinidin	procyanidin	prodelphinidin		
Monomer	1	-		-	313.3	313.6
	-		1			
Monomer	-	-	-	1	329.3	331.3
Monomer + 1 –OH in C4	-	-	-	1	346.3	347.3
Monomer-glucose (linked at flavonoid C3)	-	1	-	-	460.5	457.7/459.7
Monomer-glucose (linked at flavonoid C3)	-	-	-		492.45	489.7
Dimer – (-OH)	-	2	-	-	552.6	551.8
Dimer	-	2	-	-	569.6	569.6
Dimer	-	1	1	-	585.6	605.8
Dimer-glucose (linked at flavonoid C3)	-	2	-	-	732.7	713.7
Dimer-glucose (linked at flavonoid C3)	1	1	-	-	748.7	735.9
	-	1	1	-		
Trimer	2	1	-	-	873.9	857.5
	1	1	1	-		
	-	1	2	-		
Trimer	3	-	-	-	889.9	889.6
	2	-	1	-		
Trimer	2	-	-	1	905.9	903.6
	1	-	1	1		
	-	-	2	1		
Trimer-(linked at flavonoid C3)	2	-	-	1	1068.9	1065.3
	1	-	1	1		
	-	-	2	1		

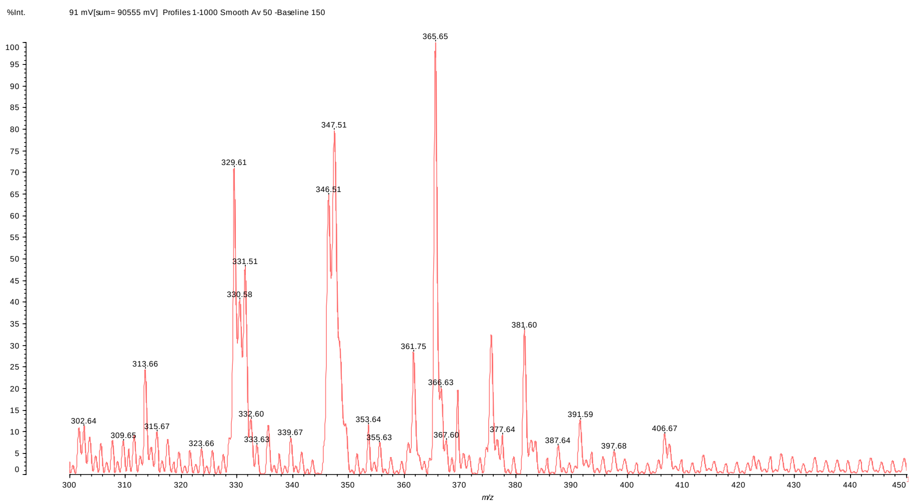


Figure 5.5a MALDI-TOF spectra of mimosa tannin/hexamine resin, range 350–450 Da

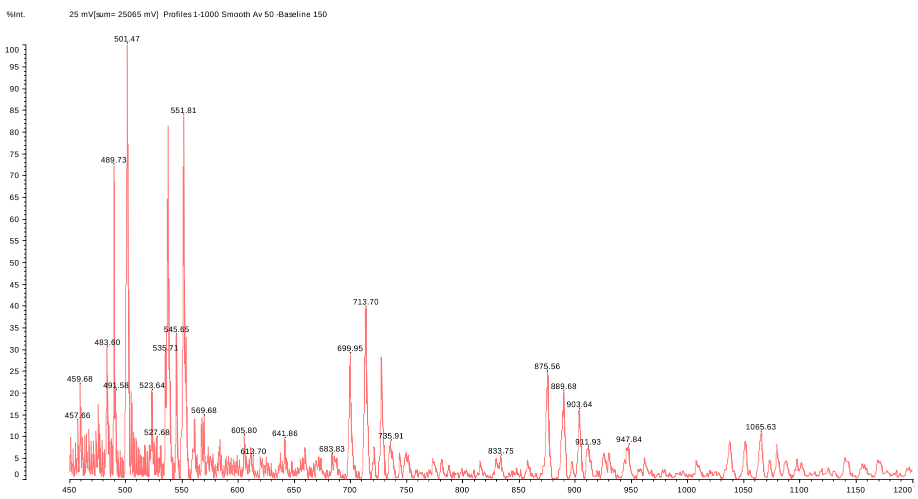


Figure 5.5b MALDI-TOF spectra of mimosa tannin/hexamine resin, range 450–1200 Da

MALDI-TOF analysis of mimosa tannin/hexamine resin added with 10% BA is shown for the molecular weight ranging from 300 to 1100 Da in Figure 5.6a and from 450 to 1100 Da in Figure 5.6b. The interpretation of the MALDI spectra yielded the series of oligomer structures shown in Table 5.7 with the calculated and experimental Da for each structure. The peak at 537.5 perfectly shows BA attachment to the flavonoid unit. Schematic representation in Figure 5.7 presents the effect of BA on the opening of pyran cycle and the formation of very reactive site. This reacted unit is ready to do reaction with other flavonoid units. In the Figure 5.6b, there is several series with a repeating increment of 162 Da. which are related to glucose unit. A free glucose molecule is 180 Da which present its Mw. But if it is a chain of glucoses (or equivalent sugars), C-OH terminal of two glucoses lose 1×–OH (17 Da) and the other one –H (1 Da) to be linked to each other with a C-O-C linkages. Thus the repeating unit in a chain of glucoses has MW of 180 -18 Da = 162 Da. So these repeating units are related to carbohydrate chains either linked to a flavonoid or a flavonoid oligomer.

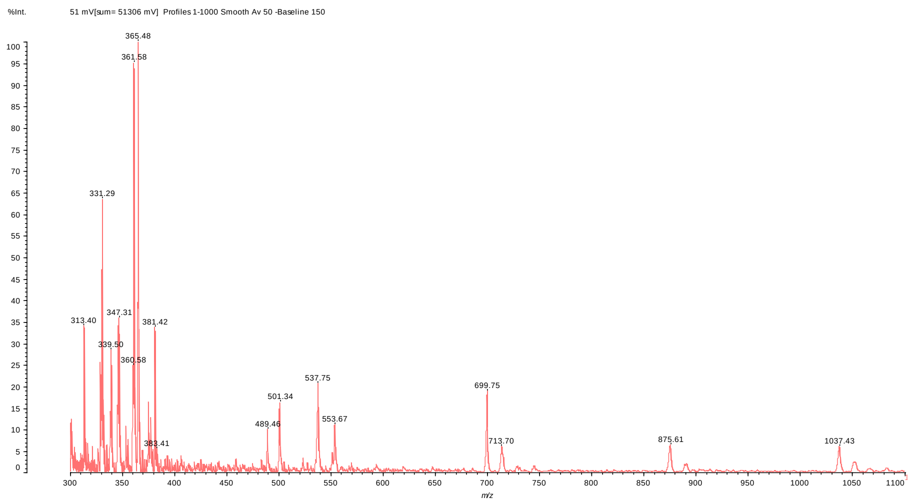


Figure 5.6a MALDI-TOF spectra of mimosa tannin/hexamine resin plus boric acid, range 300–1100 Da

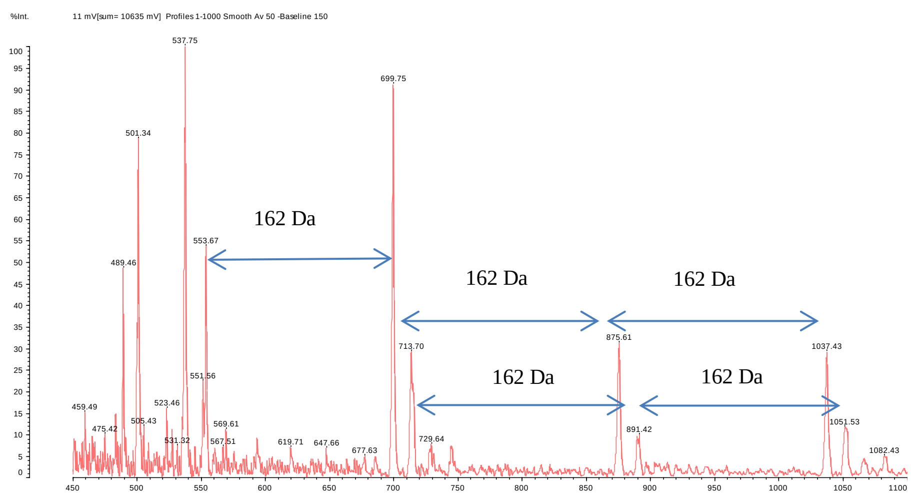


Figure 5.6b MALDI-TOF spectra of mimosa tannin/hexamine resin plus boric acid, range 450–1100 Da

Table 5.7 MALDI-TOF fragmentation peaks for mimosa tannin/hexamine added with 10% BA

Oligomer or monomer + Na^+ + 2 H	Flavonoid unit types				Calculated Mw (Da)	Experimental Mw (Da)
	prorobinetinidin	profisetinidin	procyanidin	prodelphinidin		
Monomer	1 -	-	 1	-	313.3	313.4
Monomer	-	-	-	1	329.3	329.3
Borate of Monomer -glucose (linked at flavonoid C3)	1 -	- -	- 1	- -	538.1	537.7
Borate of Monomer –glucose (linked at flavonoid C3) or Dimer	-	-	-	1	554.1	553.6
Dimer – (-OH)	-	1	-	-	552.6	553.6
Borate of Monomer –$(glucose)_2$ (linked at flavonoid C3)	- 1	- -	1 -	- -	702.1	699.75
Dimer-glucose (linked at flavonoid C3)	-	1	1	-	732.6	713.7
Dimer-$(glucose)_2$ (linked at flavonoid C3)	-	1	1	-	895.6	875.6
Dimer-$(glucose)_3$ (linked at flavonoid C3)	-	1	1	-	1058.6	1037.4

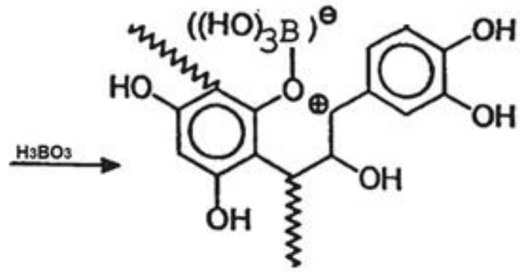


Figure 5.7 Schematic representation of BA attachment to procyanidin unit at 537.7 Da

5.5.3 TMA study

In this study thermomechanical behavior of mimosa and quebracho tannin adhesives were evaluated under the influence of BA and PMDI addition. As well as, experimental MUF adhesive which was made in the France (enstib) was studied by TMA.

5.5.3.1 **Quebracho tannin TMA study**

The study was performed in two phases: (1) the effect of tannin initial concentration, as well as the effect of PMDI addition, and (2) the thermomechanical behavior under the influence of BA addition.

Obtained TMA curves at different formulations firstly showed an increase in MOE values as a function of time and temperature. After a plateau or a very broad maximum, there is sharp decrease for all combinations starts at temperatures above 180 °C due to the start of the degradation of wood constituents (Figures. 5.8 and 5.9), as previously shown by Moubarik et al., (2013) and Osman, (2012). Figure 5.8 shows the TMA results for the MOE of joints bonded with the different quebracho tannin concentrations (but still without addition of BA). The maximum MOE increased by increasing tannin concentration from 40% to 50%, while no notable effect has been found by adding 20% PMDI resin to the glue. The maximum MOE values for 50% tannin/Hexamine alone and 50% tannin/Hexamine + PMDI were 3861.5 and 3955.23 MPa, respectively. PMDI is used in a small amount to enhance the quality of the basic adhesives such as tannins (Pizzi 1994). Osman (2012) reported the hardening reaction of the tannins/PMDI system generally produces high MOE values but it is strongly depended to the glue pH. The best results are obtained at low pH around 4. It must be mentioned that pH of the solution was around 10 in our study. The high pH was chosen because hexamine and Lewis acid perform best at such a high pH (Pichelin et al. 2006; Pizzi et al. 1995).

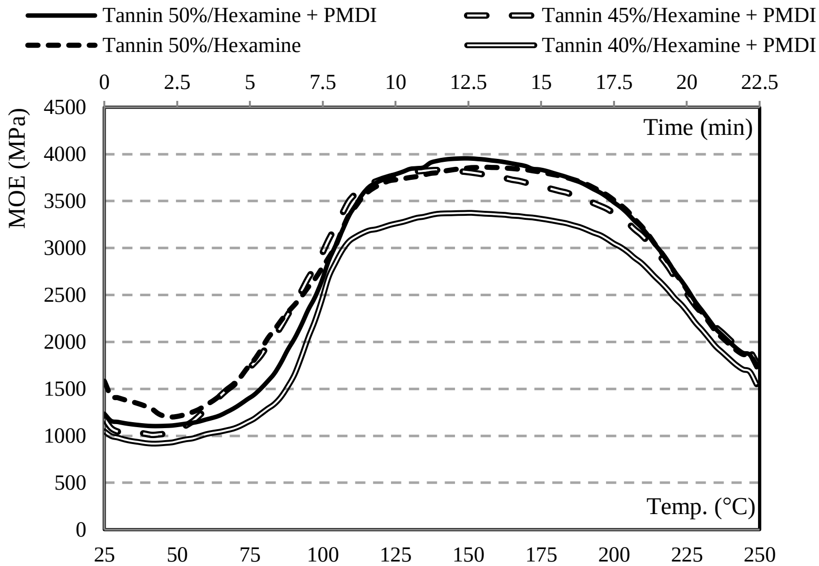


Figure 5.8 Average curve of MOE obtained by TMA testing as a function of hardening temperature and time for adhesives at different tannin concentrations with or without PMDI (without BA)

Thermomechanical analysis for BA containing adhesives showed that the addition of BA (1) lowered time and temperature of hardening, (2) and also increased MOE values of the adhesive (Figure 5.9). The reactions were faster with BA when compared with those achieved at same tannin concentration without BA. It must be noted that maximum MOE values of the adhesive increased by BA content from 2% to 4% (Figure 5.8). It was previously found that the hardening and gelation of tannin can be accelerated by BA (Efhamisis et al., 2015) when used even in very small proportions of tannin solids extracts (Meikleham et . al., 1994).

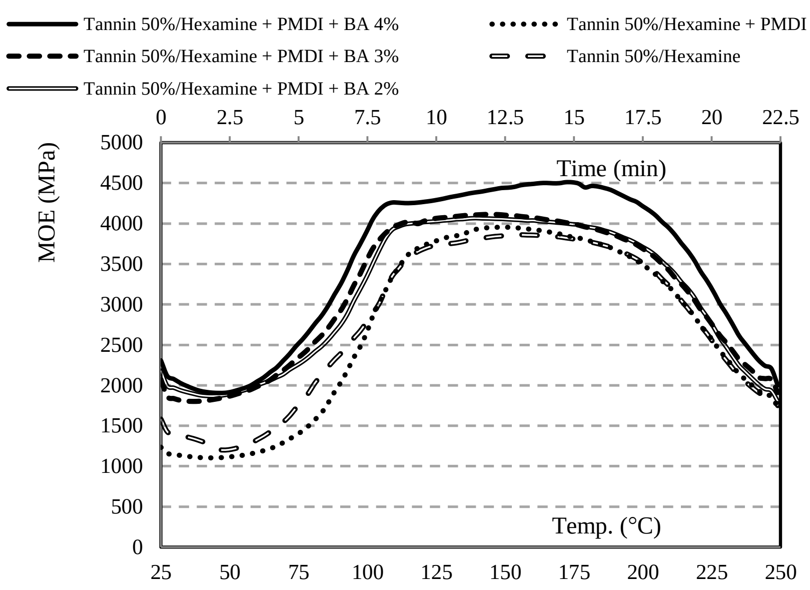


Figure 5.9 Average curve of MOE obtained by TMA testing as a function of hardening temperature and time for adhesive at 50% tannin concentration with different additives.

5.5.3.2 **Mimosa tannin TMA study**

Similar to quebracho tannin, obtained curves for mimosa tannin adhesives primarily showed an increase in MOE values as a function of time up 100-125 °C. After a very broad maximum, there was sharp decrease for all combinations starts at temperatures above 180 °C due to the thermal degradation of wood piles constituents (Figure 5.10). The maximum MOE increased by increasing tannin concentration from 45% to 50%.

The addition of 5% BA based on the tannin solids not only drastically increased maximum MOE values but also lowered time and temperature of hardening. The maximum MOE values for 50% tannin/hexamine and 50% tannin/hexamine + 5% BA were 3178 and 4074 MPa, respectively. The addition of 10% BA had the higher effect on the reduction of hardening time (or temperature) but the peak of maximum MOE decreased compared to the without BA adhesive (at 50% tannin concentration). Indeed, the addition of 10% BA acts adversely and reduces adhesive properties. The treating condensed tannin with the high amount of mineral acid, like BA, causes structural rearrangement of the tannins to insoluble phlobaphenes which changes totally the behavior of the adhesive (Foo & Karchesy, 1989; Sealy-Fisher & Pizzi, 1992). The addition of PMDI resin to the 10% BA containing adhesive at 50% tannin concentration had not any positive effect on the thermomechanical properties of the adhesive. Similar results were found in the case of quebracho tannin adhesives. The addition of PMDI did not show any improvement in TMA study.

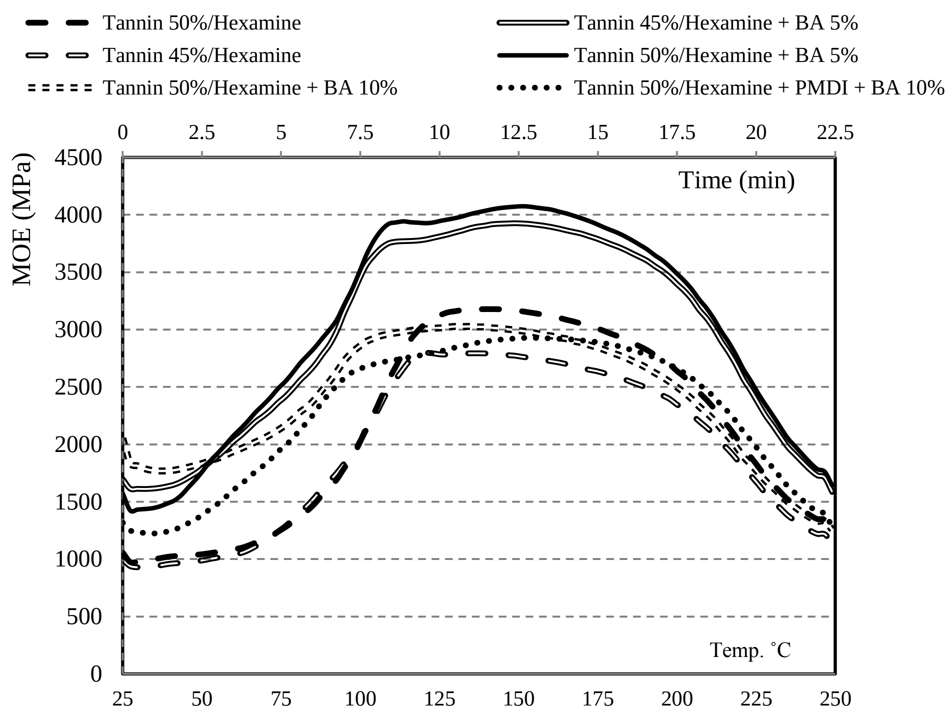


Figure 5.10 Average curve of MOE obtained by TMA testing as a function of hardening temperature and time for adhesives at varying mimosa tannin concentrations under influence of PMDI and BA addition.

5.5.3.3 **MUF TMA study**

In this study, Melamine Urea Formaldehyde (MUF) adhesive were used for gluing treated beech and poplar veneers. MUF was modified with 10% PMDI resin based on the adhesive solids. The thermomechanical behavior of experimental MUF adhesive with or without PMDI addition is shown in Figure 5.11. The trend of the curves is partly similar to the tannin adhesives. After an increase in MOE values as a function of temperature up 150 °C, a sharp decrease starts at temperatures above 180 °C due to the thermal degradation of wood piles constituents. The peak of maximum MOE is sharper than those obtained for tannin adhesives.

The addition of 10% PMDI had slightly positive effect on the obtained maximum MOE. It is worth mentioning, MUF adhesives studied here were included olive seed powder as filler which caused a few changes in the hardening trend compared to the pure MUF. In the pure MUF resin, the peak of maximum MOE is sharper and stronger (Zhou et al., 2012).

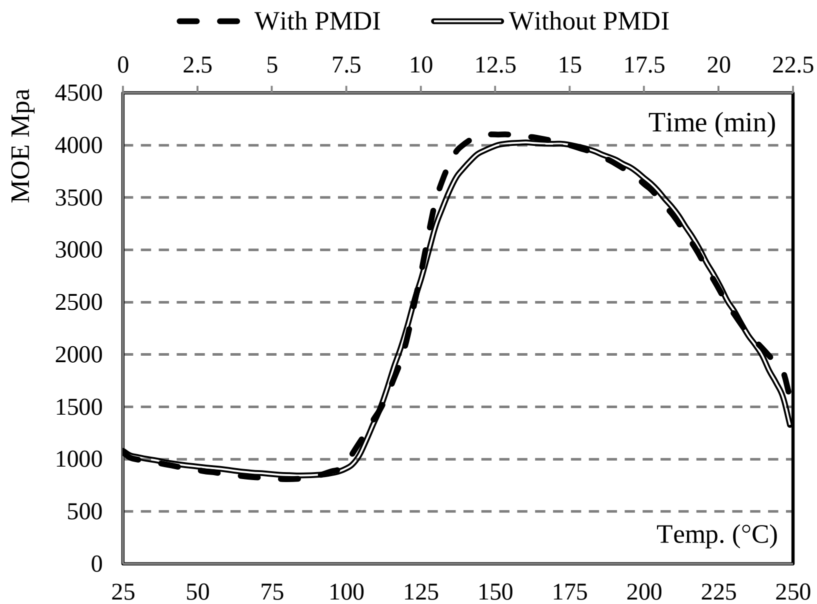


Figure 5.11 Average curve of MOE obtained by TMA testing as a function of hardening temperature and time for hardening of MUF adhesives with or without the addition of PMDI.

5.5.4 Conclusions for testing on the adhesives

1- The results of FTIR showed that adding BA can contribute more interflavonoid linkage on the B-rings by the formation of orthodiphenol complexes. The results of MALDI-TOF also perfectly showed the attachment of BA to the flavonoid units. This, in turn, can help to the opening of pyran rings and catalyze the polymerization reactions.

2- The TMA experiments showed that the addition of BA (1) lowered time and temperature of hardening, (2) and also increased MOE values of the adhesive.

CHAPTER 6: Physical Properties and tensile shear strength of plywoods

This chapter presents the results of physical features and tensile shear strength which were determined for each set of plywoods.

6.1 Glue line treated plywood

The physical and mechanical properties are separately presented for beech and poplar plywoods made with tannin adhesives.

6.1.1 Poplar plywood

6.1.1.1 Physical properties

Despite differences in the glue mixes, it did not make any trend or outstanding difference between density and moisture content (MC %) of the boards (Table 6.1).

Table 6.1 Average values for MC%, D_{od}, and $D_{12\%}$ of poplar plywood samples bonded with different quebracho tannin adhesives

	Formulations	MC (Std. dev.) %	$D_{12\%}$ (Std. dev.) kg/m^3	D_{od} (Std. dev.) kg/m^3
Tannin 40 %	Tannin/Hexamine	10.23 (0.14)	461.08 (13.94)	423.26 (18.95)
	Tannin/Hexamine + PMDI	10.24 (0.30)	451.30 (23.28)	423.64 (37.70)
	Tannin/Hexamine + PMDI + BA 2%	10.49 (0.30)	470.88 (37.64)	428.38 (21.47)
	Tannin/Hexamine + PMDI + BA 2%	10.15 (0.19)	460.94 (15.09)	433.93 (26.15)
	Tannin/Hexamine + PMDI + BA 2%	10.20 (0.20)	455.25 (26.20)	420.65 (27.74)
Tannin 45 %	Tannin/Hexamine	10.25 (0.26)	423.89 (13.56)	455.48 (18.13)
	Tannin/Hexamine + PMDI	10.00 (0.35)	464.80 (27.08)	422.08 (21.54)
	Tannin/Hexamine + PMDI + BA 2%	10.21 (0.19)	463.87 (26.35)	426.82 (24.85)
	Tannin/Hexamine + PMDI + BA 3%	10.39 (0.23)	466.54 (30.91)	434.42 (39.12)
	Tannin/Hexamine + PMDI + BA 4%	10.29 (0.21)	466.75 (25.73)	433.81 (16.29)
Tannin 50 %	Tannin/Hexamine	10.48 (0.19)	455.70 (36.83)	423.42 (29.18)
	Tannin/Hexamine + PMDI	10.55 (0.15)	469.69 (20.08)	432.01 (11.39)
	Tannin/Hexamine + PMDI + BA 2%	10.27 (0.23)	467.70 (63.78)	427.70 (46.00)
	Tannin/Hexamine + PMDI + BA 3%	10.45 (0.30)	472.03 (40.93)	437.95 (45.09)
	Tannin/Hexamine + PMDI + BA 4%	10.46 (0.33)	468.16 (23.99)	438.39 (19.82)

MC%: Moisture content; $D_{12\%}$: Conditioning density; D_{od}: Oven dry density

The oven dry (D_{od}) and conditioning ($D_{12\%}$) density values showed slightly increase by increasing the concentration of tannins and the addition of the PMDI resin into the glue mixes. The effect of adding BA was not traceable on these studied properties. It could be due to the small amount of BA which is added to the adhesives. In the other hand, the BA concentration is not varying a lot between various treatments. No significant difference was found between treatments for D_{od} and $D_{12\%}$ by a two-way ANOVA test (Annex C.1; Tables C.1).

The results obtained from the analysis of other physical properties are shown in the Figures 6.1 to 6.4.

Figure 6.1 shows the experimental data for water absorption after 2 and 24 hours at three tannin concentration levels. The water absorption values increase by increasing the time of immersion in the water. The addition of the BA and PMDI resin did not make outstanding difference between means. Two-way ANOVA test did not show considerable difference for the effect of tannin concentration and different formulations on the water absorption (Annex C.1; Table C.2).

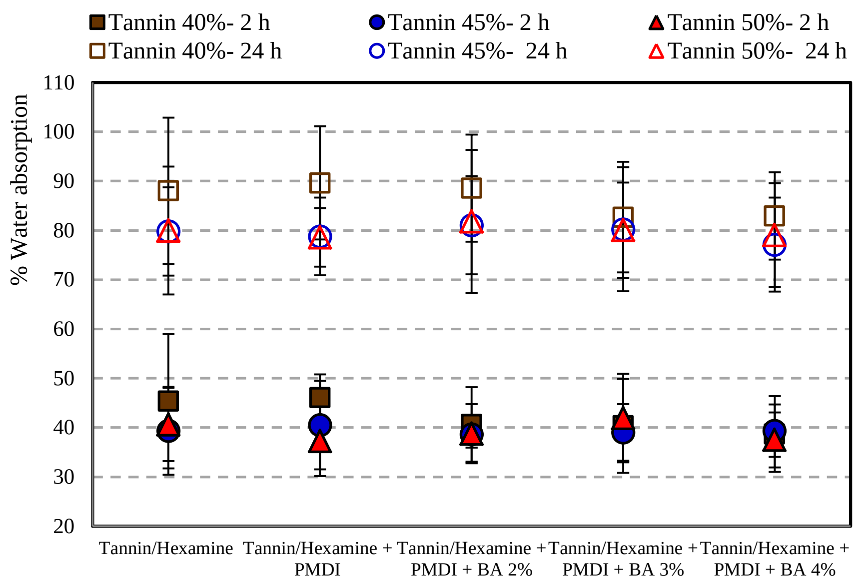


Figure 6.1 Water absorption of the poplar plywoods made with different tannin adhesives under the influence of BA and PMDI addition, after 2 and 24 hours immersion in water

The results of thickness swelling are presented in Figure 6.2. The two-way ANOVA test revealed significant difference between means (Annex C.1; Table C.3) and Duncan test grouped them in the different subsets (Annex C.1; Table C.4). Increase in the initial tannin concentration and the addition of the BA and PMDI caused obviously reduction in thickness swelling.

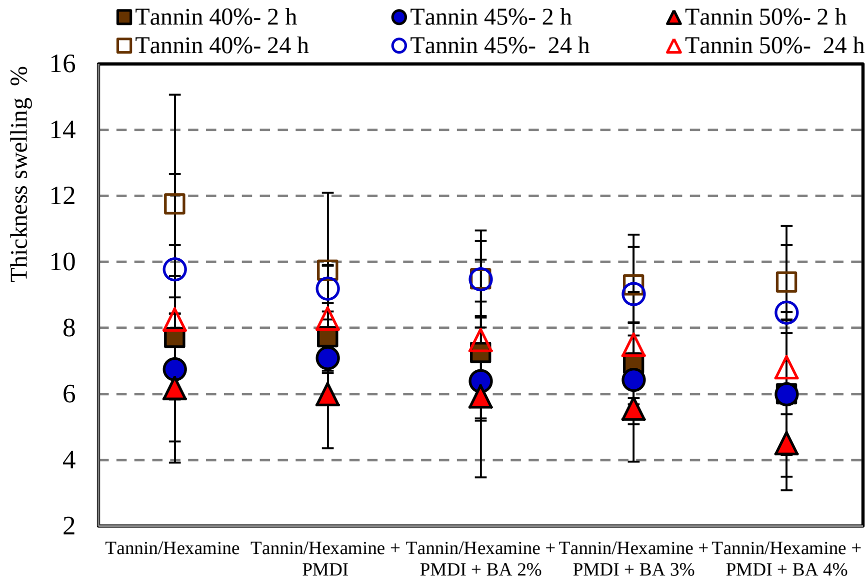


Figure 6.2 Thickness swelling of poplar plywoods made with different tannin adhesives under the influence of BA and PMDI addition, after 2 and 24 hours immersion in water

The swelling parallel to the board surface grain decreased with increase in the tannin concentration (Figure 6.3). Also the addition of PMDI and the BA had to some extent decreasing effects on the swelling. The two-way ANOVA test revealed significant difference between means (Annex C.1; Table C.5) and Duncan test grouped them in the two different subsets (Annex C.1; Table C.6). The swelling parallel to the board surface grain for the plywood samples bonded with 40% tannin/hexamine adhesives (without PMDI and BA) includes out of range data compared to the other treatments. In fact, half of the samples used for this treatment were delaminated during immersion in the water and their swelling parallel to the board surface grain was affected by core layer tangential swelling. The longitudinal swelling and shrinkage of wood is usually small, whereas radial and tangential shrinkage and swelling are more important. Plywood greatly benefits from the low longitudinal shrinkage of wood. The layers of wood veneer are glued together with the grain direction of each ply oriented perpendicular to the adjacent ply, which has the effect of restraining most radial or tangential shrinkage and swelling within the veneer plies. As a result, the rates of shrinkage for the width and length of a plywood panel are typically less than 1% (Shi & Walker, 2006). But when bonding quality is too poor surface layers of wood veneer with the grain direction are not able to control tangential swelling of the core layer.

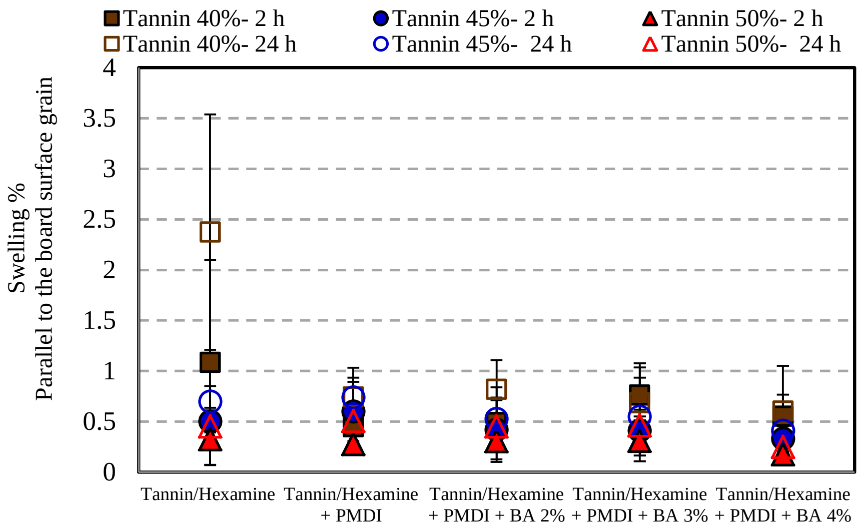


Figure 6.3 Swelling parallel to the board surface grain of poplar plywoods made with different tannin adhesives under influence of BA and PMDI addition, after 2 and 24 hours immersion in water

The results of swelling perpendicular to the board surface grain, as shown in Figure 6.4, indicate that initial concentration of tannins and the addition of PMDI as well as BA have reducing effects. The ANOVA test revealed significant difference between means (Annex C.1; Table C.7) and Duncan test grouped them in the three different subsets (Annex C.1; Table C.8). Similar to the swelling parallel to the board surface grain, the obtained value for 40% tannin/hexamine adhesives (without PMDI and BA) is out of range which is due samples delamination during immersion in the water. Also, 40% of plywood samples bonded with 45% tannin/hexamine adhesives (without PMDI and BA) were partially delaminated during experiments. No delamination was observed for plywood samples bonded with 50% tannin concentrations.

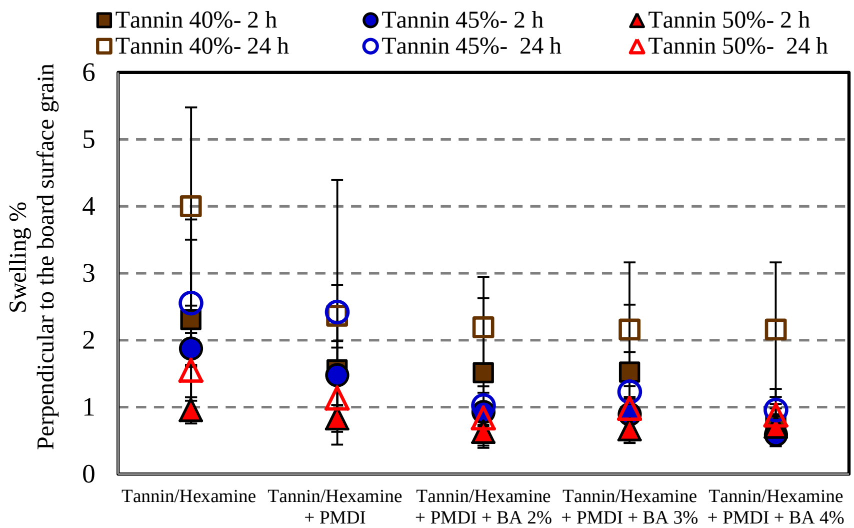


Figure 6.4 Swelling perpendicular to the board surface grain of poplar plywoods made with different tannin adhesives under the influence of BA and PMDI addition, after 2 and 24 hours immersion in water

6.1.1.2 **Tensile shear strength**

Tensile shear strength of the plywoods confirmed thermomechanical previous results (chapter 5). The shear strength (as criteria of bonding quality) increased significantly when the concentration of tannin was increased (Figure 6.5 and 6.6). A two-way ANOVA test revealed that the interactions of tannin concentration as well as the addition of BA and PMDI are statistically significant (Annex C.1; Table C.9). Tensile shear values did not meet EN 314-2 (1993) requirements (Table 6.2) for interior plywood classification in tannin/hexamine glues even with 20% PMDI (even before soaking in the water). Duncan test grouped the tensile shear values in different subsets (Annex C.1; Table C.10).

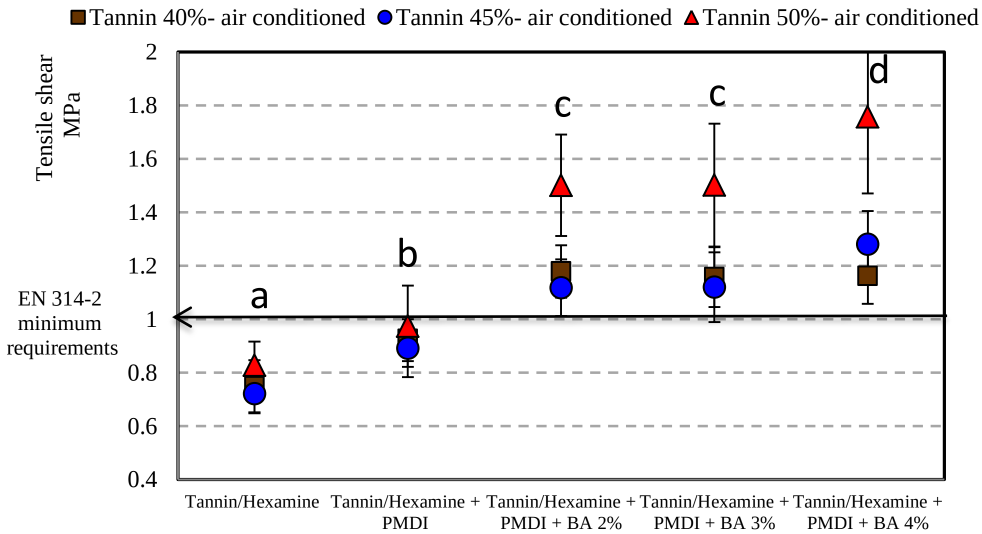


Figure 6.5 Tensile shear strength of the plywoods bonded with different adhesives of quebracho tannin in dry condition (letters show the result of Duncan grouping)

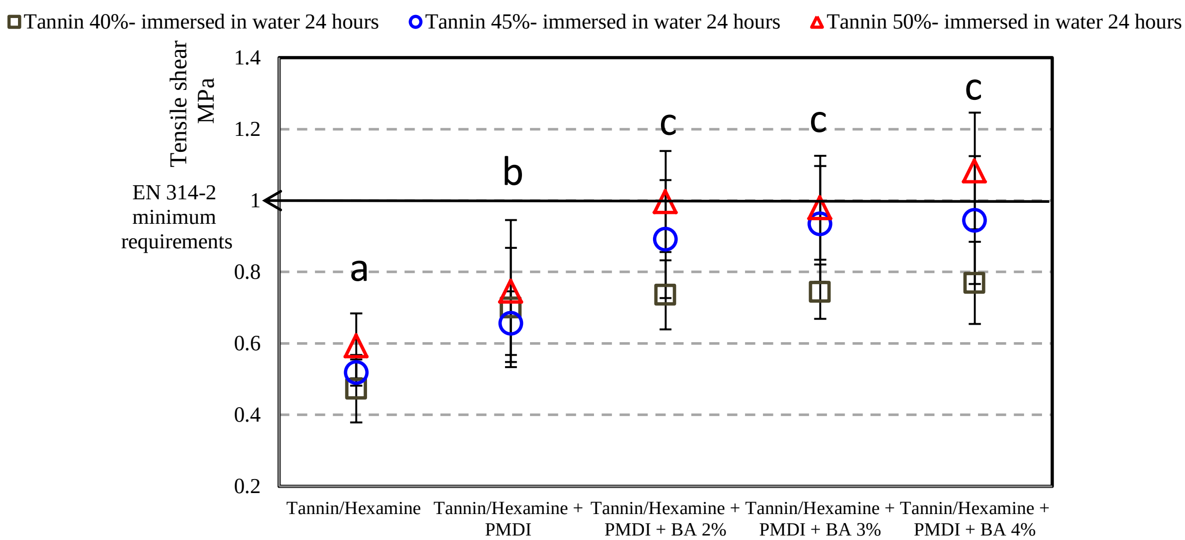
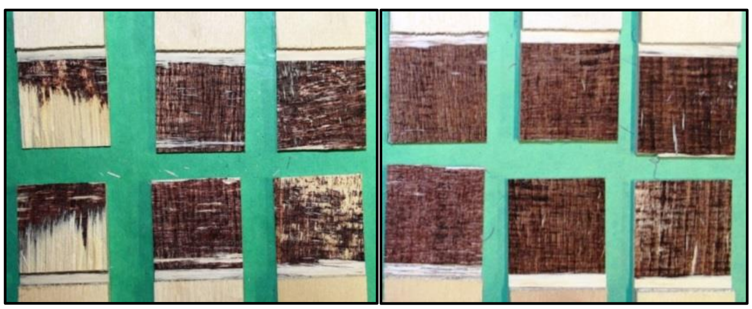


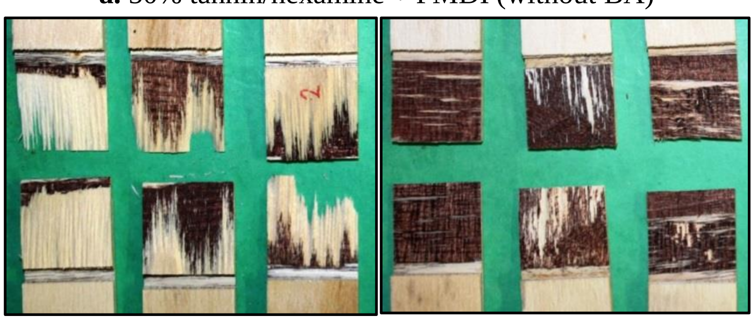
Figure 6.6 Tensile shear strength of the plywoods bonded with different adhesives of quebracho tannin after 24 hours immersion in water (letters show the result of Duncan grouping)

Following the addition of the BA, tensile shear values significantly increased which had ascending trend with increase in BA content of the glue from up to 4%. The air conditioned samples bonded with 50% tannin/ hexamine + PMDI + 4% BA showed 53.55% higher shear strength value (1.83 MPa) compared to the 50% tannin/hexamine + PMDI (0.98 MPa). In BA containing glues, tensile shear values were more than standards requirements, but it markedly reduced after soaking in water for 24 hours (Figure 6.6). According to EN 314- 2 (1993) if tensile shear value is less than 1 MPa, the mean apparent cohesive wood failure on the test area should be greater or equal 40% (Table 6.2). The wood failure percentages for immersed samples were negligible and their mean tensile shear values were less than 1 MPa for tannin glues at 40% and 45% concentrations (Figure 6.7). So, their bonding quality did not meet requirements defined. It is worth mentioning some of the plywood samples at 45% concentration still had standard shear strength in BA containing adhesive after soaking. But the plywoods made with adhesive containing 50% tannin/ hexamine + PMDI and up to 4% BA met the performance requirements for interior applications without care about wood failure in test area.

The amounts of wood failure in the tensile shear test area for some set of plywoods are shown in Figure 6.7. It can be seen that addition of BA increases wood failure in the test area. When failure occurs in the wood, it means the strength of bond lines is higher than wood strength. The higher wood failures were achieved with the higher tensile shear values.



a. 50% tannin/hexamine + PMDI (without BA)



b. 45% tannin/hexamine + PMDI + 4% BA

Figure 6.7 Wood failure in some samples of tensile shear test for poplar plywood with treated glueline, right: air conditioned status; left: after 24 hours immersion in water

The amounts of wood failure markedly decreased after the samples immersion in the water (left photos in Figure 6.7). Tannin adhesives with non-formaldehyde hardener like hexamine particularly with slow reacting tannins such as mimosa and quebracho are very sensitives against water (Pizzi et al., 1997) but they cover standard requirement for interior grade quite well.

Table 6.2 Requirement defined for bonding quality EN 314-2 (1993)

Mean shear strength f_v N/mm^2	Mean apparent cohesive wood failure %
$0.2 \leq f_v \leq 0.4$	≥ 80
$0.4 \leq f_v \leq 0.6$	≥ 60
$0.6 \leq f_v \leq 1$	≥ 40
$1.0 \leq f_v$	No requirement

6.1.2 Beech plywood

6.1.2.1 **Physical properties**

Table 6.3 presents the results obtained for the measurement of moisture content (MC %) as well as oven dry (D_{od}) and conditioning ($D_{12\%}$) density values for beech plywoods bonded with different formulations of mimosa tannin adhesive. From the results in Table, Similar to the poplar plywoods, there were no significant differences between treatments (Annex C.1; Table C.11).

The only possible source for making difference between density of treatments was solid content of the glues (Table 5.2) which were used to the gluing of veneers. But its effect was not considerable to provide any trend in the plywoods density.

Table 6.3 The average values for MC%, D_{od}, and $D_{12\%}$ of the beech plywood samples bonded with different mimosa tannin adhesives

	Formulations	MC (Std. dev.) %	$D_{12\%}$ (Std. dev.) kg/m^3	D_{od} (Std. dev.) kg/m^3
Tannin 45 %	Tannin/Hexamine	9.73 (0.17)	660.08 (16.36)	621.38 (9.51)
	Tannin/Hexamine + BA 5%	9.36 (0.18)	647.18 (20.70)	626.83 (19.64)
	Tannin/Hexamine + PMDI + BA 5%	9.25 (0.15)	642.72 (19.62)	625.92 (21.74)
	Tannin/Hexamine + BA 10%	9.24 (0.15)	648.30 (20.39)	610.95 (1.59)
	Tannin/Hexamine + PMDI + BA 10%	9.37 (0.23)	641.09 (0.20)	619.93 (18.05)
Tannin 50 %	Tannin/Hexamine	10.04 (0.14)	656.35 (15.86)	622.58 (19.04)
	Tannin/Hexamine + BA 5%	9.57 (0.10)	646.93 (17.72)	625.50 (16.43)
	Tannin/Hexamine + PMDI + BA 5%	9.65 (0.08)	646.15 (25.64)	619.50 (12.82)
	Tannin/Hexamine + BA 10%	9.611 (0.15)	651.07 (22.01)	620.78 (9.86)
	Tannin/Hexamine + PMDI + BA 10%	9.35 (0.36)	651.47 (25.34)	626.83 (19.08)

MC%: Moisture content; $D_{12\%}$: Conditioning density; D_{od}: Oven dry density

The results obtained from the analysis of other physical properties are shown in Figures 6.8 to 6.11.

Figure 6.8 shows the experimental data for water absorption after 2 and 24 hours at two tannin concentration levels. It is apparent from this figure that the addition of 5% BA did not change water absorption values compared to the base tannin/hexamine adhesive. The adhesive with 5% BA and PMDI particularly at the 50% tannin concentration reduced water absorption to some extent. With the increase in the BA content of adhesives from 5% to 10%, water absorption increased markedly. The addition of PMDI to the 10% BA containing adhesives improved water absorption. The statistical evaluations showed considerable difference between groups for water absorption by two-way ANOVA test (Annex C.1; Table C.12). Duncan test grouped the means in the two different subsets (Annex C.1; Table C.13).

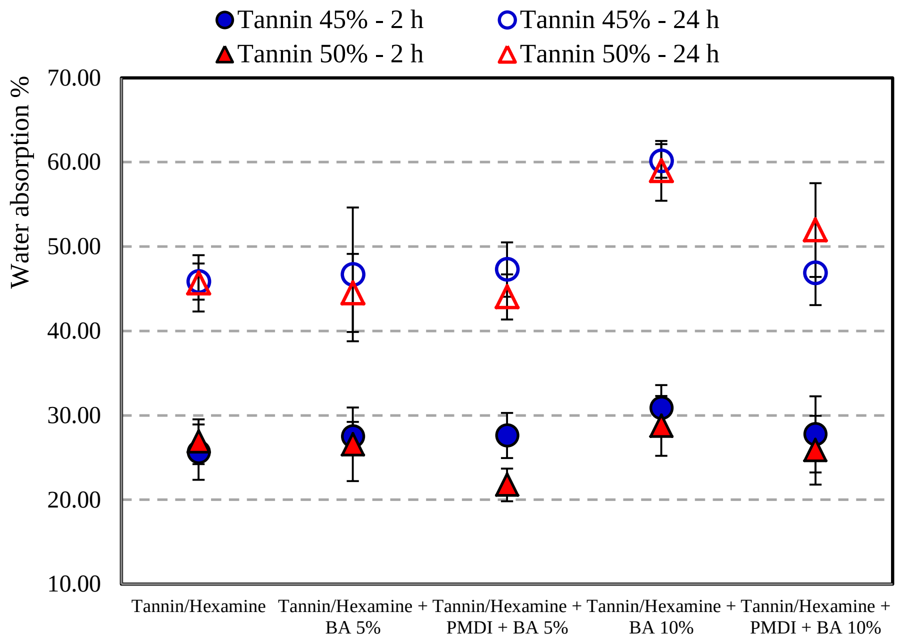


Figure 6.8 Water absorption of beech plywoods made with mimosa tannin adhesives under the influence of BA and PMDI addition, after 2 and 24 hours immersion in water

The results of thickness swelling are presented in Figure 6.9. The two-way ANOVA test revealed significant difference between means (Annex C.1; Table C.14) and Duncan test grouped them in the different subsets (Annex C.1; Table C.15). The trend of thickness swelling was same to the results of water absorption. Increase in the initial concentration of tannins caused reduction in the thickness swelling. Also, the addition of PMDI and 5% BA reduced thickness swelling. The addition of 10% BA had negative effect on the thickness swelling and caused considerable increase in its values. PMDI addition to the 10% BA containing adhesive improved slightly the negative effect of 10% BA loading into the glueline.

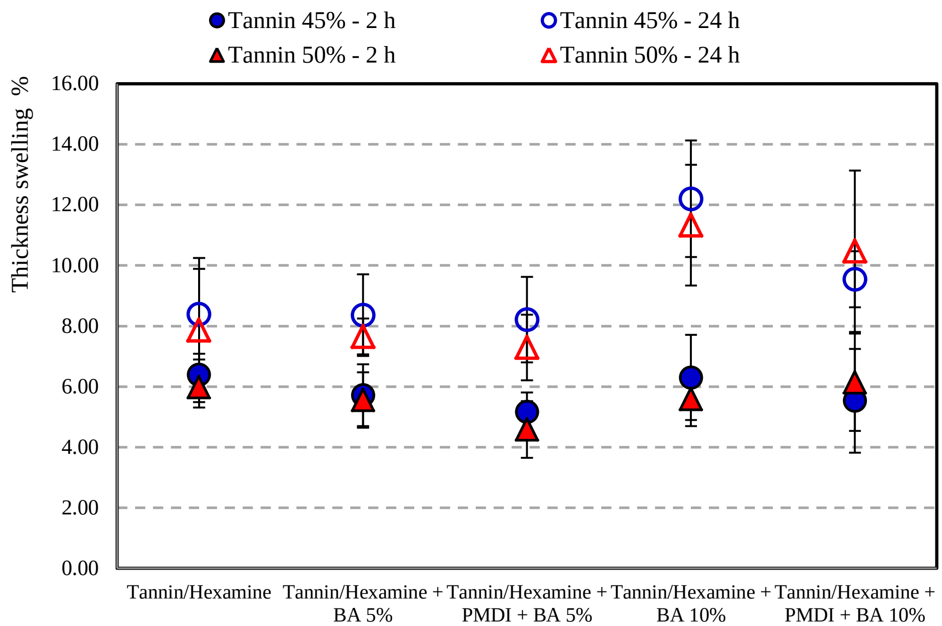


Figure 6.9 Thickness swelling of beech plywoods made with mimosa tannin adhesives under the influence of BA and PMDI addition, after 2 and 24 hours immersion in water

The results of swelling parallel and perpendicular to the board surface grain are summarized in Figure 6.10 and 6.11 respectively. The addition of PMDI and 5% BA reduced swelling in both directions. Similar to the water absorption and the thickness swelling, the values of swelling in the surface directions for 10% BA containing adhesives either with PMDI or without PMDI are distinctly out of range compared to the other treatments. All the plywood samples bonded with 10% BA containing adhesives and half of the samples bonded with 10% BA + PMDI adhesives were delaminated during soaking in the water. The results of two-way ANOVA and Duncan tests for the swelling parallel or perpendicular to the board surface grain are presented in Tables C.16-19 (Annex C.1). Increase in the solid content of the tannin from 45 to 50% was not statistically significant on the swelling for both directions. The effect of BA and PMDI addition was significant.

The values of swelling in the perpendicular direction were higher than parallel direction (in non-delaminated boards). In fact in the measuring of swelling in the surface directions of plywood, the amount of swelling in the parallel direction to the board surface grain is affected by longitudinal swelling of surface wood layers. But the amount of swelling in the perpendicular direction is affected by tangential swelling of core wood layer. The longitudinal swelling (or shrinkage) of normal wood is small and always less than 1% (Shi & Walker, 2006).

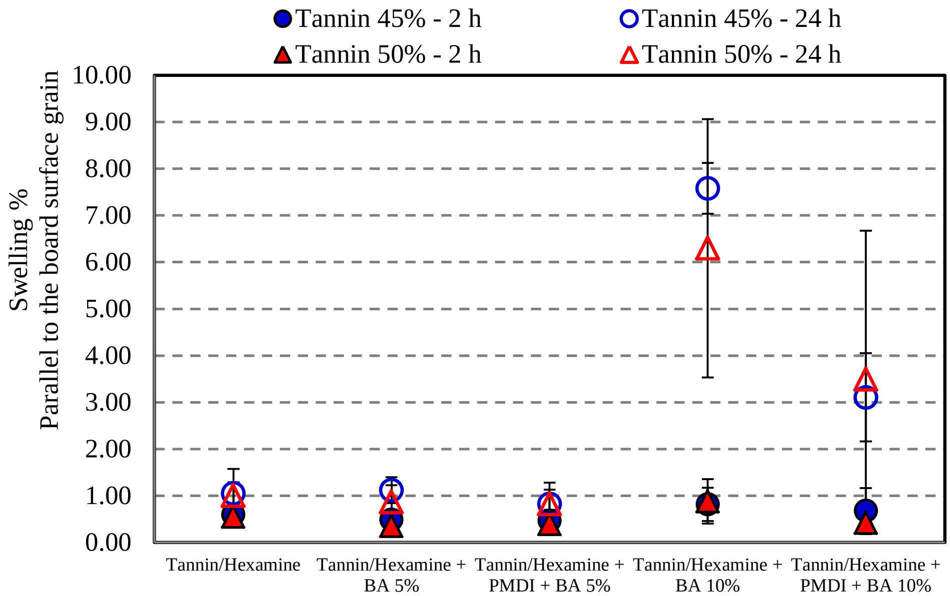


Figure 6.10 Swelling parallel to the board surface grain of beech plywoods made with mimosa tannin adhesives under influence of BA and PMDI addition, after 2 and 24 hours immersion in water

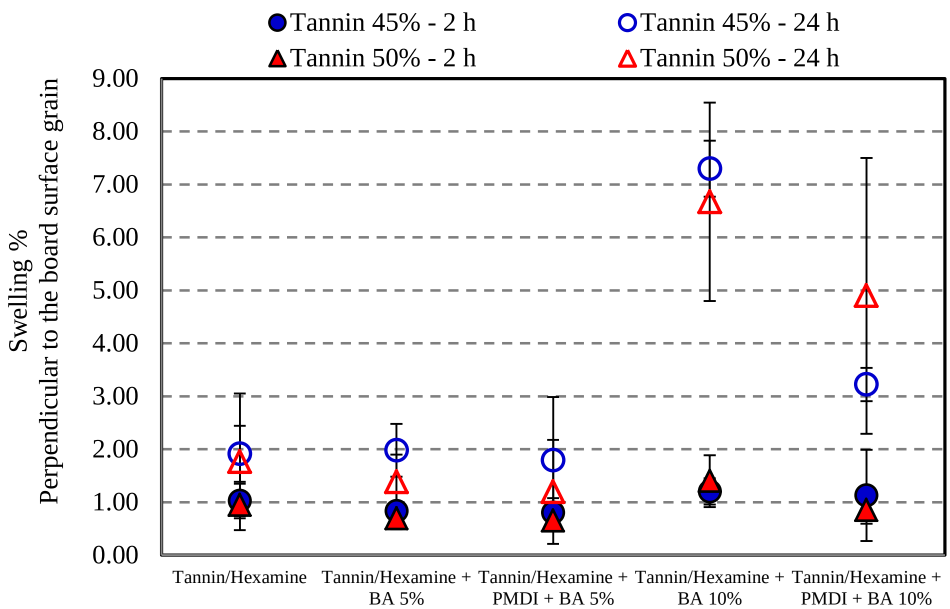


Fig. 6.11 Swelling perpendicular to the board surface grain of beech plywoods made with mimosa tannin adhesives under the influence of BA and PMDI addition, after 2 and 24 hours immersion in water

6.1.2.2 **Tensile shear strength**

Figures 6.12 and 6.13 indicate tensile shear strength of beech plywoods made with mimosa tannin adhesives in dry condition and after soaking in water respectively. The beech plywoods bonded with base tannin/hexamine adhesive at 50% concentration showed higher tensile shear value compared to the tannin/hexamine adhesive at 45% concentration.

The addition of 5% BA and PMDI resin significantly increased tensile shear strength. Two-way ANOVA test revealed significant difference between means (Annex C.1; Table C.20) and Duncan test grouped them in the different subsets (Annex C.1; Table C.21). Increase in the BA content from 5 to 10% increased tensile shear strength in dry condition. But after soaking in the water, plywood samples bonded with 10% BA (without PMDI) had tensile shear values as much as base tannin/hexamine adhesive (Duncan grouping in Figure 6.13).

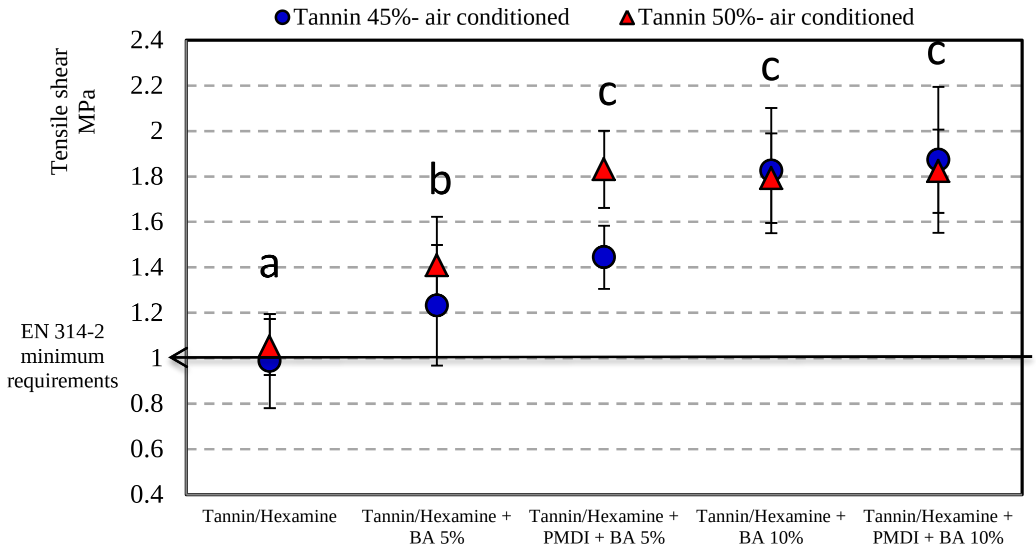


Figure 6.12 Tensile shear strength of beech plywoods made with mimosa tannin adhesives in dry condition (letters show the result of Duncan grouping)

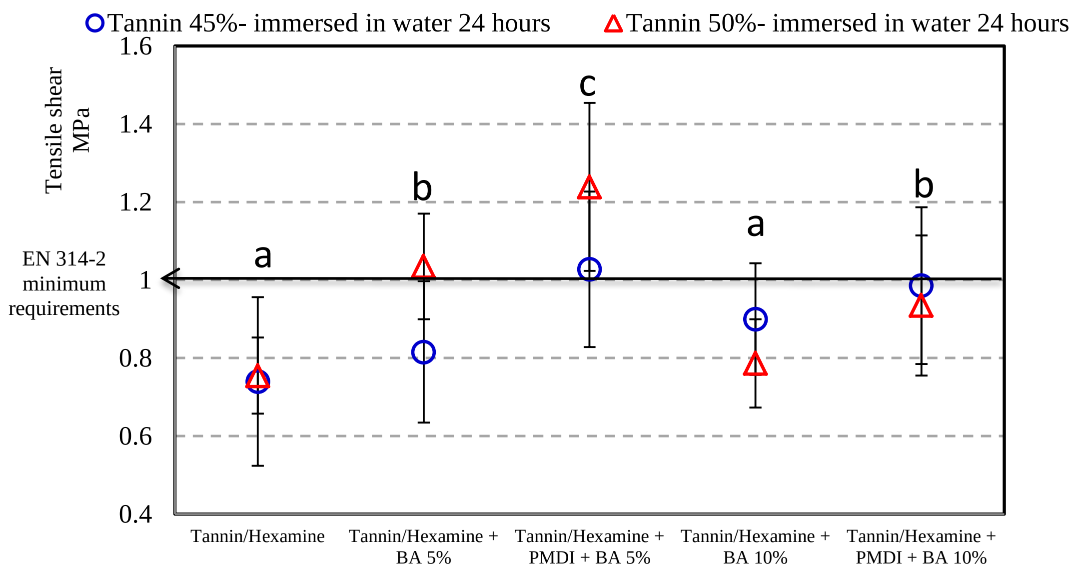


Figure 6.13 Tensile shear strength of beech plywoods made with mimosa tannin adhesives after 24 hours immersion in water (letters show the result of Duncan grouping)

All adhesives met the EN 314-2 (1993) standard requirements in dry condition with the exception of base tannin/hexamine at 45% concentration (Table 6.2). After 24 hours soaking in the water, only three formulations covered standard requirements:

1. 45% Tannin/Hexamine + PMDI + 5% BA
2. 50% Tannin/Hexamine + 5% BA
3. 50% Tannin/Hexamine + PMDI + 5% BA

The addition of PMDI into the tannin adhesives, however, did not show significant effect in the thermomechanical analysis (TMA). But the further physical and the tensile shear evaluations indicated that PMDI addition can positively improve plywoods characteristics particularly after soaking in water. The reactions of tannin with PMDI, PF or other waterproof resins is called co-polymerization reactions (Osman, 2012) which in a small amount can enhance the quality of the basic adhesives such as tannins (Pizzi 1994).

The increase in the tensile shear values (in dry condition) by the increase in the BA content from 5 to 10% were contrary to the expectations caused by TMA study. TMA studies showed that increase in BA content from 5 to 10% accelerates hardening reaction quite well but reduces also maximum achievable MOE. Though, soaking in the water prior to the tensile shear test confirmed TMA findings, where increase in the BA content from 5 to 10% caused poor bonding quality.

The amounts of wood failure in the tensile shear test area for some set of plywoods are presented in Figure 6.14.

a. 50% tannin/hexamine

b. 50% tannin/hexamine + 5% BA

Figure 6.14 Wood failure in some samples of tensile shear test for beech plywoods with treated glue line, right: air conditioned status; left: after 24 hours immersion in water

The addition of 5% BA increased wood failure in test area (Figure 6.14 b). It means the quality of bond lines getting better by 5% BA. The higher wood failures were achieved with the higher tensile shear values. The amounts of wood failure markedly decreased after the samples immersion in the water (left photos in Figure 6.14). In the 10% BA containing adhesives (with or without PMDI), the amount of wood failure was too high in dry condition but after 24 hours soaking it became null similar to the base tannin/hexamine adhesive.

6.1.3 Conclusions for the results of glue line treated boards

In summary, these results show that:

1. Increase in the tannin concentration and the addition of BA (up to 5%) and PMDI improved physical and tensile shear strength of the plywood samples.
2. The addition of 10% BA into the tannin adhesive caused imperfect physical and mechanical features.
3. The amount of wood failures in test area of tensile shear samples was visually higher by BA and PMDI addition compared to the base without additives tannin/hexamine glues.

6.2 Plywoods made of treated veneers

The physical and tensile shear strength properties are separately reported for beech and poplar plywoods made of treated veneers.

6.2.1 Beech plywood

6.2.1.1 Physical properties

Table 6.4 presents moisture content% (MC %) as well as oven dry (D_{od}) and conditioning ($D_{12\%}$) density. There was no change in the MC % associated with different treatment. But, ANOVA test revealed that there were significant differences between density of different treatments at the $p = 0.05$ level (Annex C.1; Table C.22). The Duncan test grouped oven dry and conditioning density in different subsets (Annex C.1; Table C.23). In according to the retention values (Table 5.3), significant difference was expectable in density of plywood panels made of treated veneers with tannin-boron solutions. Plywoods with non-treated core layer had reasonably less density compared to the all layers treated ones. But control plywoods and plywood panels made of treated veneers with water or BA alone solutions grouped in the same subset by Duncan test. The retention values for BA alone solutions did not provide considerable difference in density of plywoods.

Figure 6.15 shows the results obtained for water absorption after 2 and 24 hours soaking in the water. The most obvious finding to emerge from this figure is that water absorption value of plywood samples treated with 20% tannin + 1 BA is lower than other treatments. This result may be explained by the fact that the formation of the hydrophobic tannin + hexamine system (Tondi et al., 2012c) that can greatly reduce water absorption of plywood samples. Duncan test grouped this treatment in a separate subset (Annex C.1; Tables C.24 and C.25). The plywood samples with non-treated core layer had a few more water absorption. No decrease was observed in water absorption at 10% tannin concentration.

Table 6.4 Average values for MC%, D_{od}, and $D_{12\%}$ of the beech plywood samples made of treated veneers

Tannin solution %	BA %	Core layer + treated -untreated	MC (Std. dev.) %	$D_{12\%}$ (Std. dev.) kg/m^3	D_{od} (Std. dev.) kg/m^3
Control plywood			9.14 (0.50)	655.52 **a** (16.48)	624.68 **a** (22.79)
Treated with water			9.64 (0.44)	651.86 **a** (25.75)	618.80 **a** (19.67)
−	0.5	+	9.31 (0.63)	652.26 **a** (19.09)	619.75 **a** (18.61)
−	0.5	_	9.47 (0.5)	657.13 **a** (24.36)	620.05 **a** (25.54)
10	0.5	+	10.10 (0.55)	721.16 **c** (14.98)	660.14 **bc** (15.05)
10	0.5	_	10.01 (0.89)	690.86 **b** (29.47)	651.79 **b** (18.01)
−	1	+	8.90 (0.53)	658.55 **a** (25.38)	621.69 **a** (36.00)
−	1	_	9.81 (0.42)	659.04 **a** (17.23)	618.26 **a** (27.46)
20	1	+	10.00 (0.57)	738.41**d** (20.22)	693.31**d** (22.94)
20	1	_	9.48 (0.48)	732.48 **cd** (25.47)	683.96 **cd** (19.58)

MC%: Moisture content; $D_{12\%}$: Conditioning density; D_{od}: Oven dry density; Letter (a, b, c, d) show the results of Duncan grouping

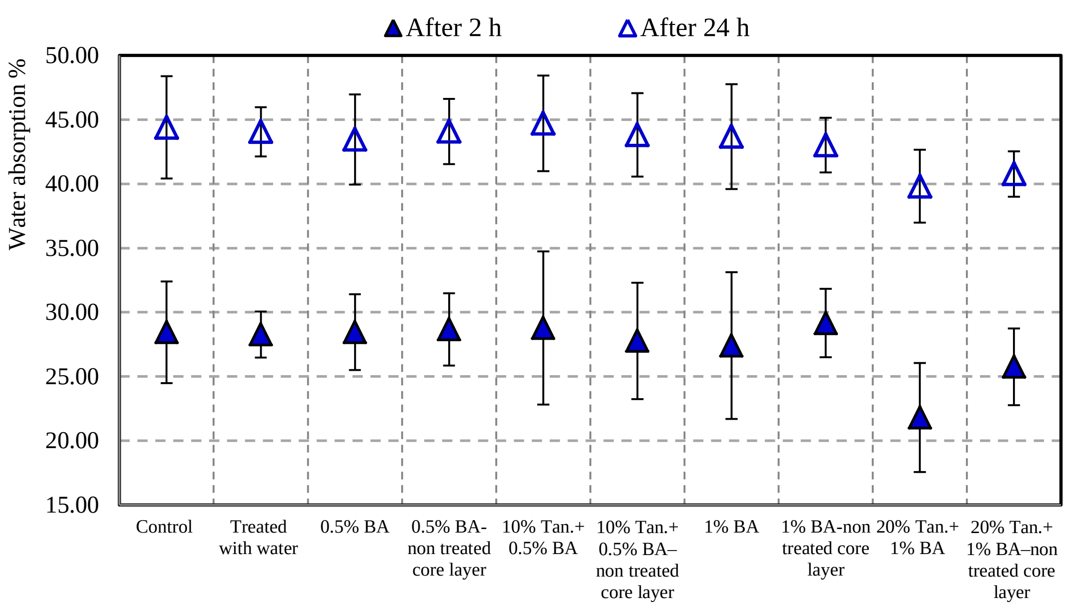


Figure 6.15 Water absorption of the beech plywoods made of treated veneers, after 2 and 24 hours immersion in the water

The results of the thickness swelling are shown in Figure 6.16. The plywood samples made from treated veneers with 20% tannin + 1% BA showed relatively lower thickness swelling particularly after 2 hours immersion. However, no significant difference was found between treatments for the values of thickness swelling (Annex C.1; Table C. 26). The amount of thickness swelling for beech plywood bonded with good performance tannin adhesives like 50% tannin + 5% BA with or without PMDI are comparable with data obtained here for beech plywoods bonded with MUF adhesive (Figure 6.9).

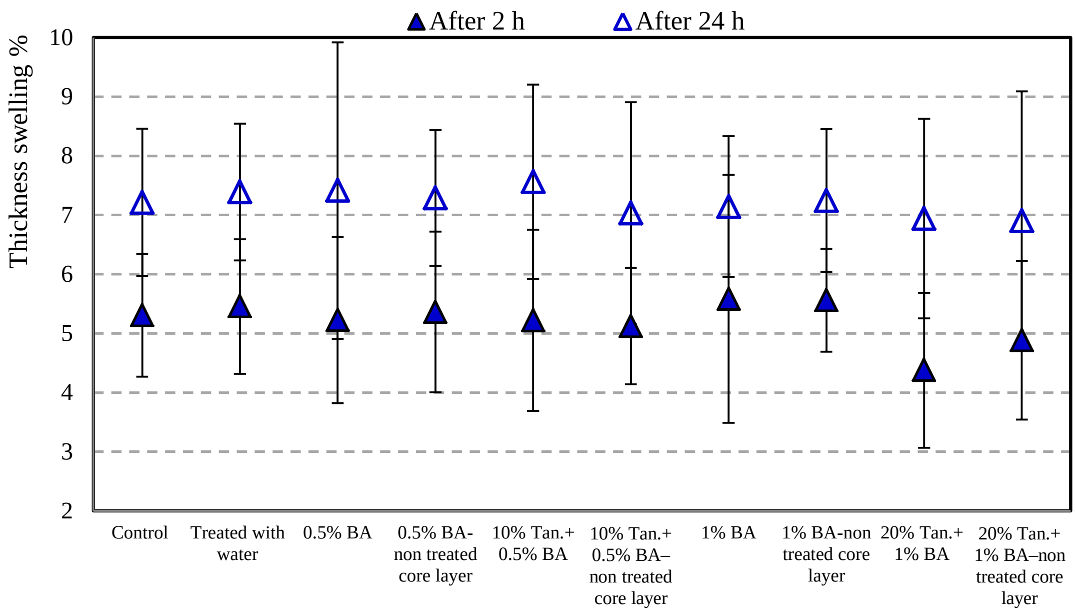


Figure 6.16 Thickness swelling % of the beech plywoods made of treated veneers, after 2 and 24 hours immersion in the water

The swelling parallel as well as perpendicular to the board surface grain are illustrated in Figure 6.17 and 6.18, respectively. The values of swelling in the surface directions were slightly changed between treatments. The average values of swelling for parallel directions were ranged from 0.3 to 0.6 % and from 0.8 to1.20 % for perpendicular direction after 2 and 24 immersion in the water. None of these differences were statistically significant (Annex C.1; Tables C.27 and C.28).

The data obtained for beech plywoods bonded even with good performance tannin adhesives were a few higher than these ranges (Figures 6.10 and 6.11). This means MUF adhesive provides better dimensional stability by restricting wood layers swelling (or shrinkage).

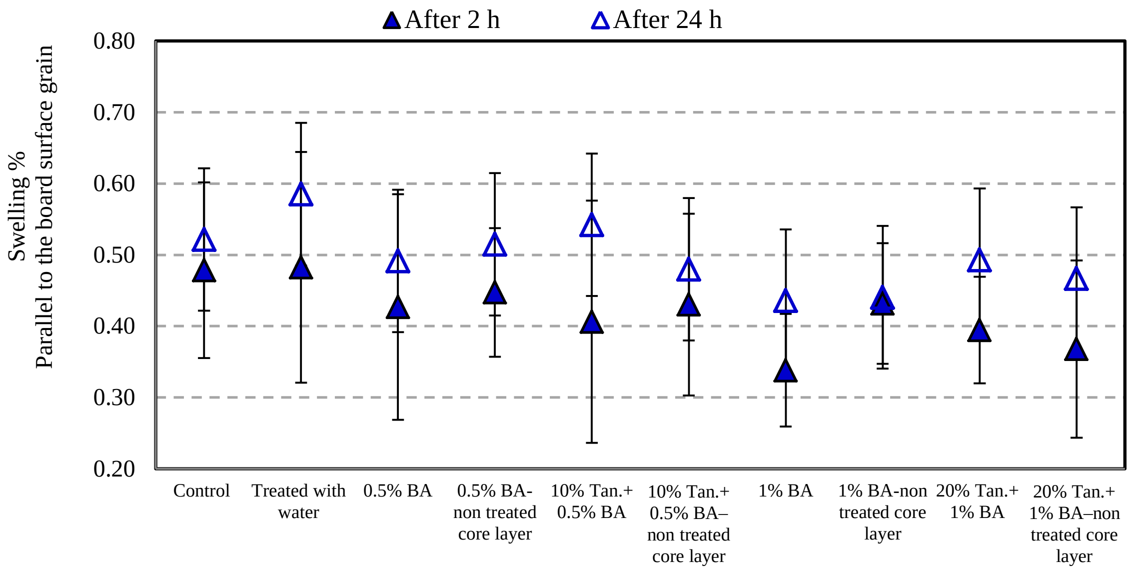


Figure 6.17 Swelling parallel to the board surface grain of beech plywoods made of treated veneers, after 2 and 24 hours immersion in water

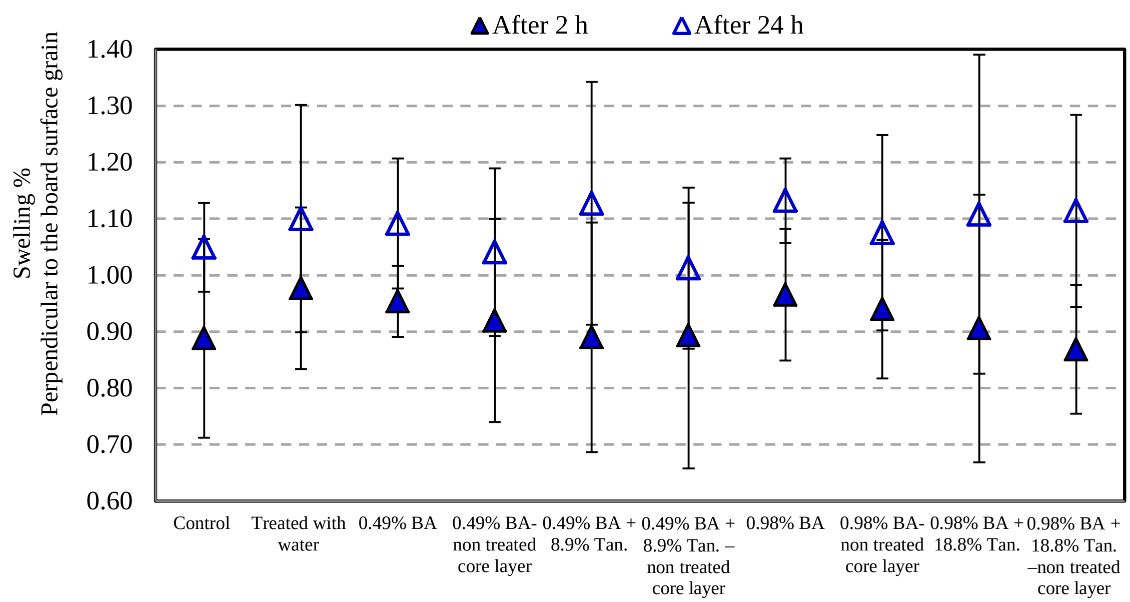


Figure 6.18 Swelling perpendicular to the board surface grain of beech plywoods made of treated veneers, after 2 and 24 hours immersion in water.

6.2.1.2 **Tensile shear strength**

The results obtained from the tensile shear evaluations between treatments are presented in Figure 6.19. Since plywood panels with treated veneers and bonded with MUF adhesive were considered for humid place uses (bond class 2), The measurement of tensile shear were done with three pre-treatment on the samples according to the EN 314-1 (2004). The ANOVA test revealed that there are significant differences between the varying treatments (Annex C.1; Table C.29). Duncan test grouped treatments in the various subsets (Annex C.1; Table C.30). The treatment of wood veneers with tannin-boron solutions apparently decreased tensile shear values and caused poor bonding quality. The results of Duncan test for tensile shear values after 24 hours immersion are shown in Figure 6.19. The plywood samples treated with 20% tannin + 1% BA showed the minimum tensile shear values compared to the other treatments and Duncan test grouped this treatment in the separate subset. The samples with non-treated core layer showed higher strength compared to the all layers treated ones. The data obtained for plywood samples in 1% tannin + 0.5% BA, also, showed less tensile shear values compared to the control plywoods. It seems possible that these results are due to the formation of solid hydrophobic tannin-boron network on the surface of pre-treated layers which consequently reduces adhesive contact with the surface of wood layers. On the other hand, the tannin resin causes the surface of the wood smoother and subsequently decreases the roughness for the grip of the adhesive. These results match those reported in an earlier study (Tondi et al., 2012b). It was reported that bonding potential of beech wood treated with tannin-boron solutions was decreased and the shearing resistance diminished when more preservative was penetrated into the wood.

The plywoods made of treated veneers with BA alone solutions did not affect tensile shear strength and presented values as much as control samples. This result seems to be consistent with other researches which found addition of optimal BA into the MUF adhesive (Bridaux et al., 2001; Lesar et al., 2011) or treatment of wood veneers with borate compounds (Colakoglu et al., 2003) did not have a negative impact on the performance of the glue lines. On the contrary, some properties were even improved such as compression strength parallel to the grain, hardness and pull-out strength of screw perpendicular to surface.

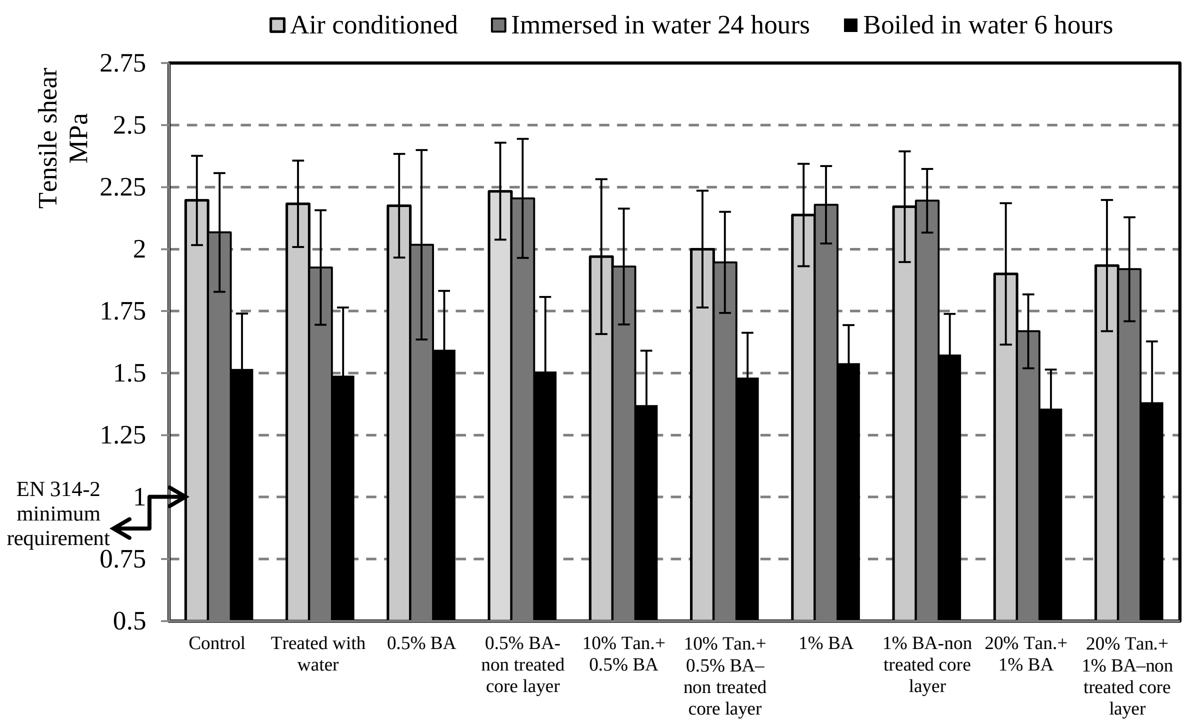
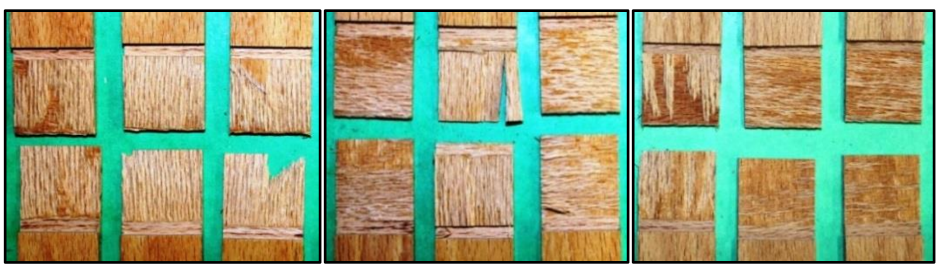


Figure 6.19 Tensile shear strength of beech plywoods made of treated veneers, with different pre-treatment prior testing (letters show Duncan grouping result)

The tensile shear strength of plywoods was decreased significantly after soaking in the cold water and particularly after 6 hours boiling. But still the values of tensile shear for all treatments were higher than the minimum standard requirements even after 6 hour boiling (Table 6.2). The minimum obtained tensile shear was corresponding to the plywood treated with 20% tannin + 1% BA after boiling.

The data recorded for plywoods treated with BA alone solution at 1% concentration showed slightly more tensile shear after soaking in the cold water. A possible explanation for this might be due to increase in wood elasticity by soaking in the water. Another possible explanation for this could be positive effect of BA on the curing of MUF resin and consequently better performance during immersion. Indeed, BA in standalone formulation is easily able to diffuse from the veneers to the adhesive in the gluing process.

The amounts of wood failure in the tensile shear test area for some set of beech plywoods are presented in Figure 6.20. It can be seen that treatment of veneers with tannin-boron system decreased wood failure in the test area compared to the control plywoods (Figure 6.20b). The higher wood failures were achieved with the higher tensile shear values. The amounts of wood failure markedly decreased after the samples immersion in the water (photos in the center) and after 6 boiling (photos in the right). In the 20% tannin+ 1% BA treatment, the amount of wood failure became null after boiling. Whereas, control samples still shows notable wood failure after boiling.



a. control plywood

b. 20% Tannin + 1% BA

Figure 6.20 Amount of the wood failure in some samples of the tensile shear test for beech plywoods, right: air conditioned status; center: after 24 hours immersion in water; left: after 6 hours boiling

It is worth mentioning, there is no need to take care about wood failure in the test area according to EN 314-2 (1993), when the value of tensile shear strength is greater than or equal to 1 MPa (Table 6.2). The tensile shear values for all beech plywoods made with MUF adhesive were higher than 1 MPa. All the beech plywoods from the different treatment met standard requirement for bond class 2.

6.2.2 Poplar plywood

6.2.2.1 **Physical properties**

Table 6.4 presents moisture content (MC %) as well as oven dry (D_{od}) and conditioning ($D_{12\%}$) density. Similar to the beech plywoods, there was no significant difference in the MC% associated with different treatment. The same trend similar to the beech plywoods was observed for D_{od} and $D_{12\%}$. The D_{od} and $D_{12\%}$ were increased in the plywood samples treated with tannin-boron system. ANOVA test revealed that there are significant differences between $D_{12\%}$ density of different treatments (Annex C.1; Table C.31). There were no significant differences in D_{od} between treatments, since the high standard deviation (Annex C.1; Table C.31). The result of Duncan test is shown for $D_{12\%}$ in Table C.32 (Annex C.1).

Table 6.5 Average values for MC%, D_{od}, and $D_{12\%}$ of the poplar plywood samples made with treated veneers

Tannin solution %	BA %	Core layer + treated -untreated	MC (Std. dev.) %	$D_{12\%}$ (Std. dev.) kg/m^3	D_{od} (Std. dev.) kg/m^3
Control plywood			9.67 (0.32)	481.25 **a** (30.10)	439.03 (31.05)
Treated with water			9.30 (0.36)	479.50 **a** (33.47)	437.80 (30.10)
−	1	+	10.01 (0.32)	484.93 **a** (23.41)	440.16 (22.69)
10	1	+	10.42 (0.26)	511.01 **ab** (23.77)	467.50 (20.31)
10	1	−	10.41 (0.26)	490.56 **b** (24.34)	449.61 (17.46)

MC%: Moisture content; $D_{12\%}$: Conditioning density; D_{od}: Oven dry density; The letters (a, b) show the results of Duncan grouping

Figure 6.21 shows the results of water absorption after 2 and 24 hours soaking in the water. No significant differences were observed between treatments (Annex C.1; Table C.33). The average range of water absorption for poplar plywoods with tannin adhesive (Figure 6.1) were higher than values obtained here for plywoods with MUF adhesive. The MUF adhesive seems to be an effective barrier against water penetration (Bridaux et al., 2001).

The results of the thickness swelling are shown in Figure 6.22. Similar to the beech plywoods, no significant differences were observed under influence of treatments (Annex C.1; Table C.34). The values of thickness swelling for poplar plywoods bonded with the best performance tannin adhesive (50% tannin+ 20% PMDI+ up to 4% BA) was as much as data obtained here for poplar plywoods bonded with MUF adhesive (Figure 6.2).

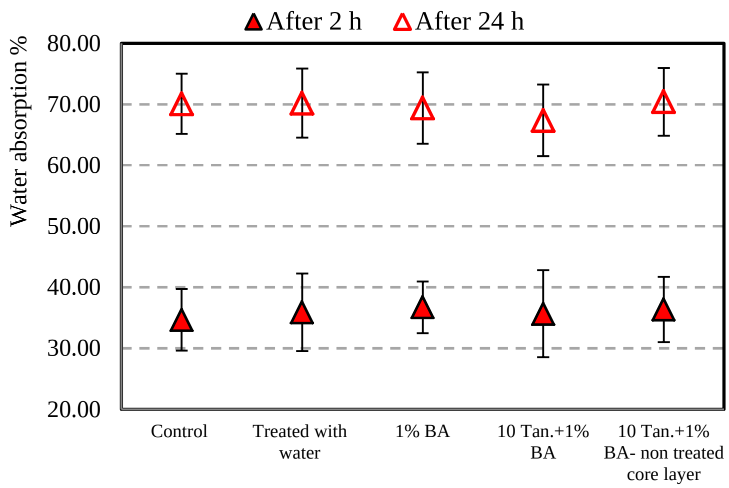


Figure 6.21 Water absorption of poplar plywoods made of treated veneers, after 2 and 24 hours immersion in water

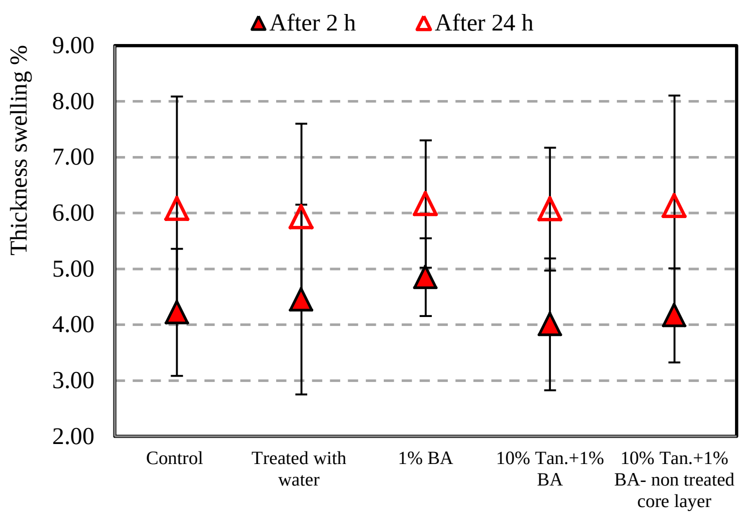


Figure 6.22 Thickness swelling of the poplar plywoods made of treated veneers, after 2 and 24 hours immersion in water

The swelling parallel as well as perpendicular to the board surface grain are illustrated in Figures 6.23 and 6.24, respectively. Similar to the beech plywoods, the values obtained here were slightly changed between treatments. None of these differences were statistically significant (Annex C.1; Tables C.35 and C.36). The average values of swelling for parallel directions were ranged from 0.2 to 0.5 % and from 0.5-0.9 % for perpendicular direction between 2 and 24 hours soaking. The value of swelling in surface directions for poplar plywood bonded with the best performance tannin adhesive (Figures 6.3 and 6.4) is as much as data obtained here for poplar plywoods bonded with MUF adhesive.

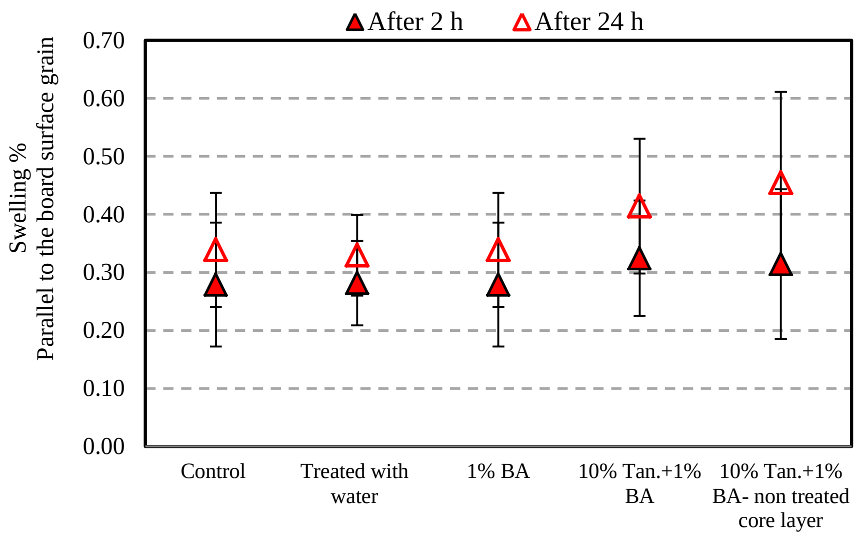


Figure 6.23 Swelling parallel to the board surface grain of the poplar plywoods made of treated veneers, after 2 and 24 hours immersion in the water.

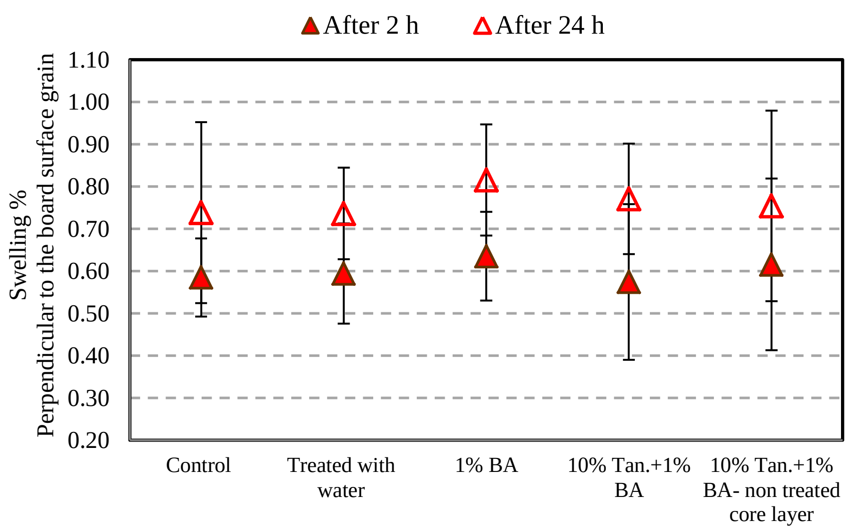


Figure 6.24 Swelling perpendicular to the board surface grain of the poplar plywoods made of treated veneers, after 2 and 24 hours immersion in the water

6.2.2.2 **Tensile shear strength**

The results obtained from the tensile shear study are presented in Figure 6.25. Similar to the beech plywood, the measurement of tensile shear were done with three pre-treatment prior testing. Despite some differences between treatments, there were not detected any statistically significant differences between treatment in each pre-treatment conditions by one-way ANOVA test (Annex C.1; Table C. 37). The treatment of wood veneers with tannin-boron solution slightly decreased tensile shear values and caused poor bonding quality.

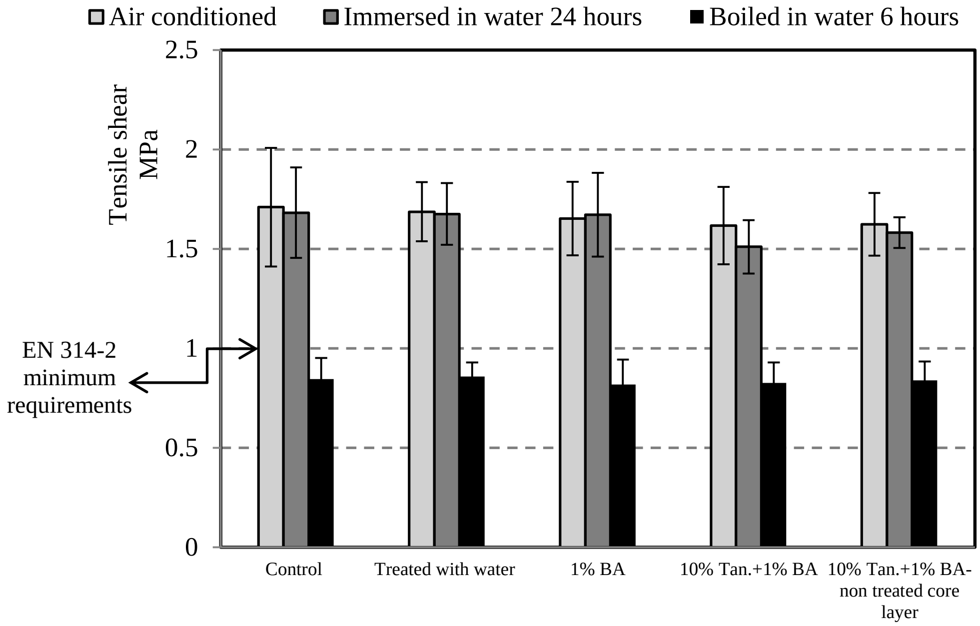


Figure 6.25 Tensile shear strength of poplar plywoods made of treated veneers with different solutions, with three different pre-treatment prior testing.

The tensile shear strength of plywoods was decreased slightly after soaking in the cold water (not statistically significant). But 6 hours boiling in the water caused dramatic decrease in the tensile shear values. To the extent that the amounts of tensile shear were diminished to the sub-standard levels (Table 6.2). So based on the bonding quality none of the treatments met standard requirements for using in bond class 2 conditions. On the other hand the amounts of wood failure in the test area were so small (Figure 6.26).

It should be noted that MUF adhesive used for gluing poplar veneers was industrial type and supplied by an Iranian company. But MUF adhesive used for gluing beech veneers was experimentally produced in the laboratory. The type and the amount of additives were kept same for both adhesives (filler, hardener, and PMDI resin). But the solid content of pure MUF was different between two adhesives. The solid content of experimentally produced MUF and industrially ones were 61% and 53%, respectively. Because of poor bonding quality, the effect of treatment with tannin-boron system on tensile shear strength was not possible to study after boiling in the water. Indeed, all of the poplar plywoods were partially delaminated during boiling and they rendered same values for tensile shear.

The tensile shear values of beech plywoods were considerably higher than poplar plywoods even in air conditioned status. A possible explanation for this might be firstly due to poor MUF adhesive which was used for gluing poplar veneers. Secondly, poplar wood has less density and consequently less mechanical resistance compared to the beech wood. The amounts of wood failure in the test area of samples were too much in air conditioned samples (Figure 6. 26). So, the inherent resistance of wood may play an important role on the obtained values when the amount of wood failure is high.

The amounts of wood failure in the test area of control and treated plywoods are presented in Figure 6.26. The higher wood failures were achieved with the higher tensile shear values. The amounts of wood failure were decreased slightly after the samples immersion in the water (photos in the center). But, the amount of wood failure became null after 6 hours boiling (photos in the right) for both control and treated plywoods.

a. control poplar plywood

b. 10% tannin + 1% BA

Figure 6. 26 Amount of the wood failure in some samples of the tensile shear test, left: air conditioned status; center: after 24 hours immersion in water; right: after 6 hours boiling

6.2.3 Conclusions for the results of veneers treated boards

Overall, these results indicate that:

1. The treatment of veneers with tannin-boron solutions caused significant increase in the density of plywoods. This was due to the considerable loading of tannin-boron resin in wood layers by vacuum/pressure methods. The MC% did not show any trend or outstanding difference between treatments.
2. Treatment of veneers with tannin-boron system or standalone BA solutions not only did not affect adversely the physical properties. But also, the beech plywoods made of treated veneers with 20% tannin+1% BA showed lower water absorption compared to the other treatment.
3. Tensile shear values of beech and poplar plywood decreased to some extent in the plywoods made of treated veneers with tannin-boron systems. The negative effect of tannin based solution on the bonding potential was the higher when tannin concentration was the higher. Despite the negative effect (on tensile shear) of tannin-boron systems, all the beech plywoods met minimum standard requirements for bond class 2. But the poplar plywoods did not met standard requirements. The MUF adhesive which was used for gluing of poplar veneers was different and caused poor bonding quality.

CHAPTER 7: Biological results – Fungal and termite tests

This chapter renders biological experiments results included fungal and termite tests, before and after leaching procedure, for each set of plywoods.

7.1 Fungal test

7.1.1 Virulence samples and controls

Table 7.1 shows the results of fungal test for virulence and solid wood controls. The average weight loss for the virulence controls meet the minimum weight loss required for beech virulence sample (20%) according to ENV 12038 (2003). Thus, the fungal test was valid as the fungal strain was virulent. The average weight losses for poplar controls and beech virulence controls clearly show that poplar and beech species are of low durability according to the natural durability classification of XP Cen TS 15083-1 (2006). The size controls are massive wood but with the size of plywoods use in the experiments. They showed much higher humidity and weight loss at the end of the test than controls massive wood with standard size. The size controls have larger size and less thickness than controls with standard dimensions which play a role in moisture uptake in the sample and creating a favorable environment for the fungal growth. In particular for *Trametes versicolor* that needs moisture for growth more than brown rot fungi like *Coniophora puteana* (Schmidt, 2006).

Table 7.1 Fungal test results of virulence samples as well as, controls of beech and poplar solid woods. Attack by the white rot fungus *Trametes versicolor*

Type of sample	Humidity Average at the end of the test (Std. dev.) %	Average weight loss (Std. dev.) %
Virulence controls of beech wood (50 × 25 × 15 mm^3; L × R × T)	43.90 (8.66)	23.98 (4.14)
Poplar wood controls (50 × 25 × 15 mm^3; L × R × T)	39.94 (9.43)	23.16 (2.59)
Size controls of poplar wood (50 × 50 × 6 mm^3; L × R × T)	164.42 (65.03)	45.31 (2.90)
Size controls of beech wood (50 × 50 × 6 mm^3; L × R × T)	136.48 (58.58)	47.12 (9.64)

7.1.2 Plywood samples with treated glue line

The plywoods made with tannin adhesive were considered for bond class 1 (indoor applications). In this condition of service the risk of attack by surface molds or by staining or wood-destroying fungi is insignificant. The attack by wood-destroying insects, including termites and beetles, is possible but the frequency and importance of this risk depends upon the geographical region (EN 335, 2013). Despite of this fact, the effect of BA addition into the tannin glue was evaluated on fungal attack before and after leaching as preliminary study and collecting data.

7.1.2.1 **Poplar plywoods**

7.1.2.1.1 **Before leaching**

Figure 7.1 shows the results of fungal test before leaching for poplar plywoods with treated glue line. The humidity of the samples at the end of the test is shown in Table D.1 (Annex D). The humidity of poplar plywoods was approximately similar to size controls of poplar wood (above 100%). No hydrophobic effect was observed in association with plywood configuration on the humidity. The humidity of the poplar plywood and size controls was higher than poplar solid wood controls with standard dimensions. Since the values of weight losses were more than 3% and humidity of the samples were higher than 20%, there is no need to pay attention to confirm the results of test (ENV 12038, 2003).

The plywood samples which were made with adhesives without BA did not show any resistance against fungus and their weight loss was as much as poplar size controls. No effect was observed by the addition of PMDI.

Following the addition of the BA, a significant decrease in the weight loss was recorded. This result is significant at the p = 0.05 level (Annex C.2; Table C.38). The result of Duncan test for the weight loss values are shown in Table C.39 (Annex C.2). The treatments without BA (with or without PMDI) were grouped together in the same subset. Increase in tannin concentration (from 40 to 50%) and BA content (from 2 to 4%) increased durability. The minimum weight loss was 7.37 % associated with 50% tannin+ PMDI+ 4% BA The BA was loaded just into the gluelines but it caused drastic decrease in the weight loss values. The treatment must insure an average weight loss of 3% to be efficient based on the ENV 12038 (2003).

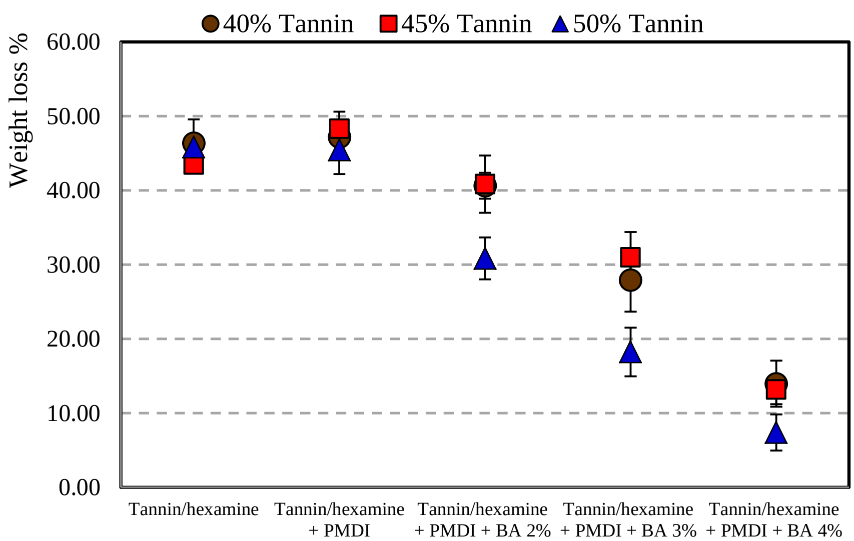


Figure 7.1 Average weight losses of poplar plywoods with treated glue line before leaching. Attack by the white rot fungus *Trametes versicolor*

Tannin adhesive retained mobility of BA to diffuse in the plywood profile and acted as fungistatic. The chelate complex reactions of borate anion with oxidized co-enzymes of fungi probably lead to the biostatic effects of borate through metabolic inhibition (Lloyd et al., 1998).

The maximum retention and uptake for BA was 0.20% (w/w) and 0.81 kg/m^3 in the plywood samples made with 50% tannin/hexamine+ PMDI+ 4% BA (Table 5.1) which improved drastically durability against fungal attack. Toxic threshold values of BA for solid wood to be fully support against *Trametes versicolor* was reported around 0.2% (w/w based on the wood weight) and 0.76 kg/m^3 (Drysdale, 1994; Lloyd et al., 1998).

7.1.2.1.2 **After EN 1250-2 (1995)**

The average weight loss after exposure to fungal attack after leaching procedure according to EN 1250-2 (1995) is presented in Figure 7.2. The fungal test after leaching was done just on the plywood samples made with tannin adhesive at 45% and 50% concentrations. The plywood samples at 40% tannin concentration were highly delaminated during leaching test which was due to the poor bonding quality (Figure 6.6).

The humidity of the samples at the end of the test is summarized in Table D.2 (Annex D). It was higher than 150% for all the samples with exception of ones made with 50% tannin/hexamine-PMDI- 4% BA (105%).

The weight loss of the samples bonded with without BA adhesives were as much as before leaching values. In the BA containing adhesives the leached samples present a higher weight loss values than the non-leached ones. It can be explained based on the some free BA that did not take place in the tannin polymerization reactions pending the pressing time (Tondi et al., 2012a) and was washed out by leaching procedure. But still the plywood samples made with BA containing adhesives showed the lower weight loss which was significant at p value = 0.05. The results of ANOVA test and Duncan grouping is exhibited in Tables C. 40 and C.41 (Annex C.2). The best protective performance after leaching was associated to the plywood samples made with 50% tannin/hexamine+ PMDI+ 4% BA.

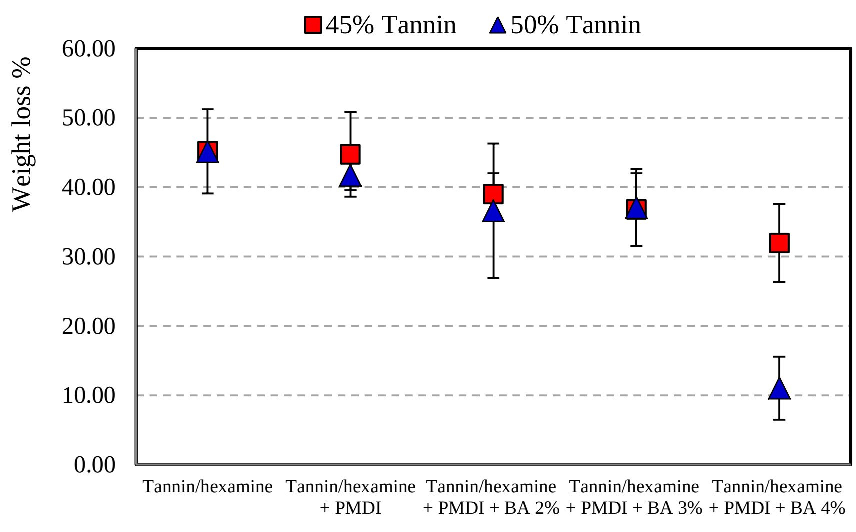


Figure 7.2 Average weight losses of poplar plywoods with treated glue line after leaching test according to EN 1250-2. Attack by the white rot fungus *Trametes versicolor*

The leachate waters of the initial leaching periods were brownish particularly in the lower tannin concentration and when BA was not in the adhesive. It can be due to the dissolution of low-molecular weight tannin oligomer (Tondi et al., 2012a). Following the addition of the BA into the adhesive, it aids to opening of the rings and formation of high- molecular weight tannin (Pizzi., 2006) which can be more resistant to leach out. In this systems the BA is non-covalently bonded to the tannin but retains sufficient mobility that allows it to work as fungicide (Thevenon, et al., 2010).

7.1.2.1.3 **After EN 84 (1997)**

The results of fungal test after EN 84 (1997) leaching procedure are summarized in Figure 7.3. As can be seen, the weight loss of the samples bonded with the adhesives containing BA is as much as without BA samples. No significant differences were found between treatments by ANOVA (Table C.42). The humidity of the samples at the end of the test is summarized in Table D.3 (Annex D). It was more than 150% for all treatments. EN 84 (1997) leaching guidelines is the strictest leaching procedure in the European norm. It looks that all the boron has leached out during the leaching.

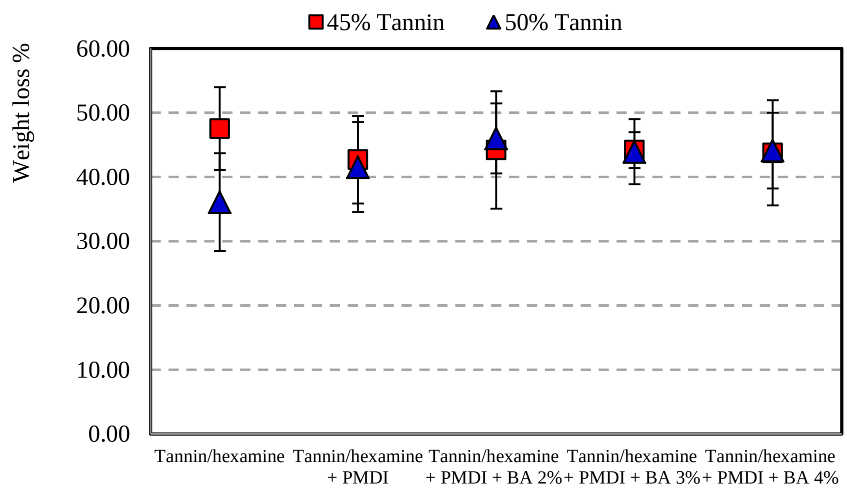


Figure 7.3 Average weight losses of poplar plywoods with treated glue line after leaching test according to EN 84. Attack by the white rot fungus *Trametes versicolor*

The values of the weight loss after exposure to the fungal attack were compared at 50% tannin concentration before and after leaching tests in Figure 7.4. From the figure we can see that there is no trend or outstanding different between varying treatments after EN 84 leaching test.

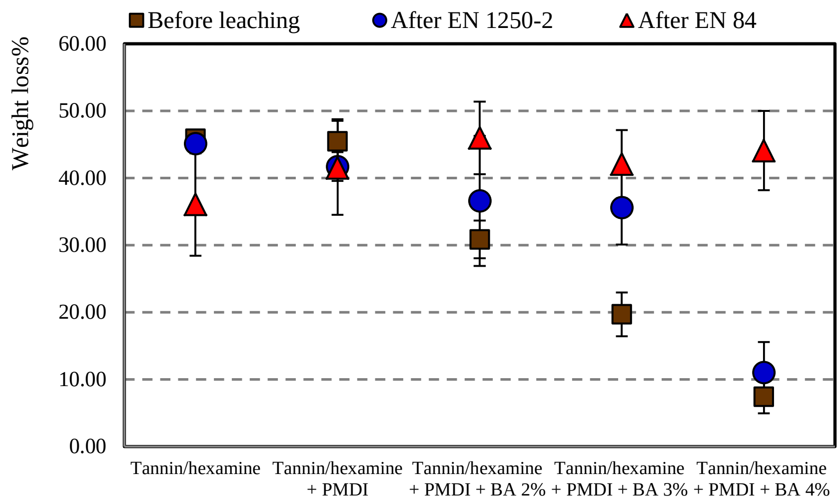


Figure 7.4 Average weight loss of poplar plywoods with treated glue line before and after leaching, at 50% tannin concentration. Attack by the white rot fungus *Trametes versicolor*

7.1.2.2 **Beech plywood**

7.1.2.2.1 **Before leaching**

The results of fungal test before leaching for beech plywoods with treated glue line are presented in Figure 7.5. The plywood samples which were made with adhesives without BA did not show any resistance against fungus and their weight loss was as much as beech size controls (Table 7.1).

The results of humidity at the end of the test (Annex D; Table D.4) showed that the humidity of control plywoods (tannin/hexamine glue) even was higher than for size controls (Table 7.1). But the plywood samples including BA and PMDI in the gluelines had considerably lower humidity at the end of test. The minimum humidity was associated to plywood samples made with 50% tannin/hexamine+ PMDI+ 5% BA (59.8%). Since the weight losses were more than 3% and humidity of the samples at the end of test are higher than 20% so the test is valid.

Following the addition of BA, a drastic decrease in the weight loss was obtained. This result is significant at the p = 0.05 level (Annex C.2; Table C.43). The result of Duncan test for the weight losses is shown in Table C.44 (Annex C.2). Despite apparent differences, the treatments containing different level of BA were grouped together in a same subset and the treatment without BA in another one. This is due to high standard deviation of weight loss values which does not let Duncan test to recognize more subsets.

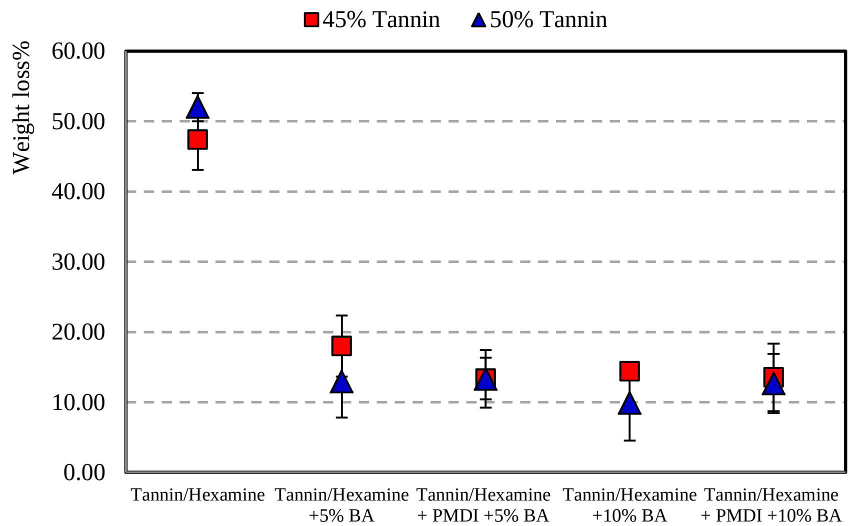


Figure 7.5 Average weight losses of beech plywoods with treated glue line before leaching. Attack by the white rot fungus *Trametes versicolor*

The minimum weight loss obtained for beech plywoods was 9.87% in 50% tannin/hexamine-10% BA. The amount of the BA retention in this treatment was 2.15 kg/m^3 (0.36% w/w). While, the minimum weight loss obtained for poplar plywoods was 7.37% in 50% tannin/hexamine-PMDI- 4% BA. The amount of retention in this treatment was 0.81 kg/m^3 (0.20% w/w).

It should be noted that tensile shear strength was lost with 10% BA loading in the glue line (Figure 6.13). The treatments including 10% BA in the glue line were delaminated during fungal test (16 weeks). The delamination of plywood layers may accelerate degrading rate by fungus and causes more weight loss. But still the beech plywoods with good performance glue lines which met standard requirements for bond class 1 (Figure 6.13) and containing 5% BA have more weight loss compared to the poplar plywoods. The minimum retention obtained for beech plywood was 0.93 kg/m^3 (0.14% w/w) which is still higher than maximum retention achieved for poplar plywood (0.81 kg/m^3; 0.20% w/w).

This inconsistency may be due to lower BA uptake based on the oven dry weight of wood in the beech plywoods. The amount of retention (kg/m^3) is higher but the uptake (w/w %) based on the weight is lower. Indeed, the efficacy of retention is depended on the wood density (Schoeman & Lloyd, 1998). The poplar wood is lighter and more porous than the beech wood. Another explanation for this phenomenon may be due to the easier diffusion of boron in poplar than in beech.

Despite all these, 5% BA addition resulted in drastic decrease in the weight loss compared to the controls, without negative effect on the bonding quality and physical properties. It was used only in the glue line but presented good performance against fungal attack.

7.1.2.2.2 **After EN 1250-2 (1995)**

The results of fungal test after EN 1250-2 (1995) leaching procedure are presented in Figure 7.6. The weight loss of the controls (without BA) was approximately as much as before leaching.

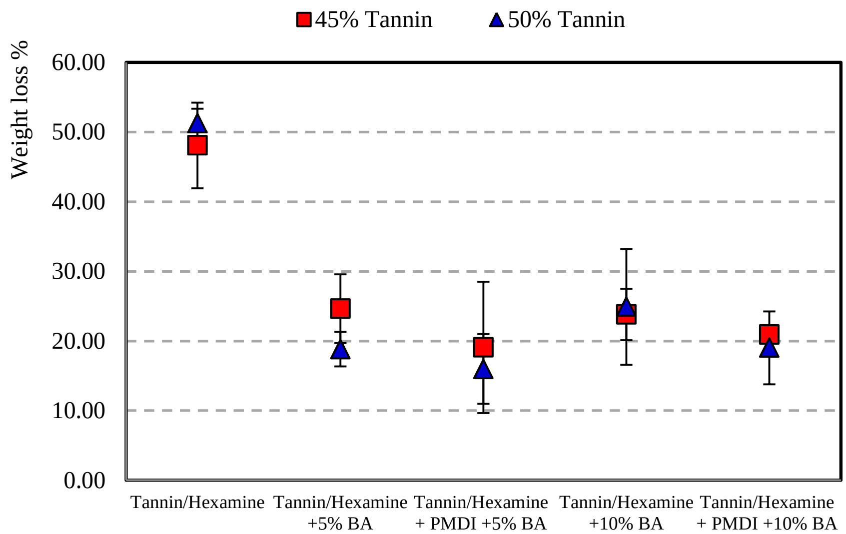


Figure 7.6 Average weight losses of beech plywoods with treated glue line after EN 1250-2. Attack by the white rot fungus *Trametes versicolor*

The result of humidity at the end of test is summarized in Table D.5 (Annex D). The samples including BA and PMDI in the glue line still showed considerably lower humidity (below 100%) compared to the control plywoods with no additives in the glue (above 150%). Similar to the poplar plywoods, BA containing plywoods presented a higher weight loss values than unleached ones. What is interesting in these data is that the plywoods including 5% BA showed lower weight loss than 10% BA containing ones. It was contrary to its previous state before leaching. The plywoods with 10% BA in the glue were highly delaminated during leaching test which could contribute leaching of BA with the higher rate. The ANOVA test revealed that differences between treatments are significant (Annex C.2; Table C.45) and further Duncan test grouped the means in the different subsets (Annex C.2; Table C.46).

The leachate waters of the initial leaching periods were brownish which was darker in the control adhesives than for adhesives included PMDI and BA. Also the plywoods with 10% BA presented darker leachate waters. It was due to the delamination of the layers and the poor bonding quality. Plywood samples made of 50% tannin/hexamine- PMDI- 5% BA showed the best result after EN 1250-2 (1995).

7.1.2.2.3 **After EN 84 (1997)**

The result of fungal test after EN 84 (1997) leaching procedure is shown in Figure 7.7. As can be seen, the weight loss of the samples made with the adhesives containing 5% BA is as much as without BA controls. Duncan test grouped them together in a same subset (Annex C.2; Tables C.47 and C.48). Similar to the poplar plywoods, it seems that all the boron was leached out by EN 84 in these treatments.

The result of moisture content at the end of test showed that the humidity of all the samples was approximately above 100% (Annex D; Table D.6).

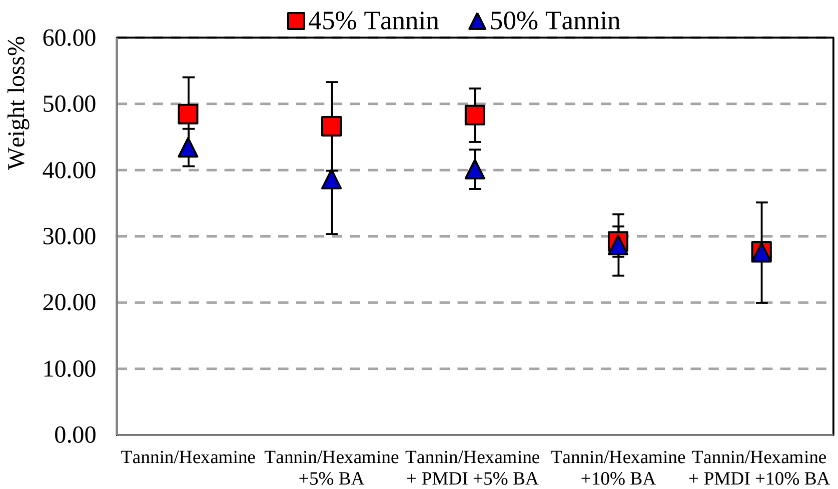


Figure 7.7 Average weight losses of beech plywoods with treated glue line after EN 84. Attack by the white rot fungus *Trametes versicolor.*

The results of weight loss after exposure to fungal attack were compared at 50% tannin concentration before and after leaching test in Figure 7.8. The samples including 10% BA showed lower increase in the weight loss after EN 84 compared to the 5% BA. It seems that most of the leachable boron can wash out by EN 1250-2 according to delamination of samples with 10% BA in the glue lines.

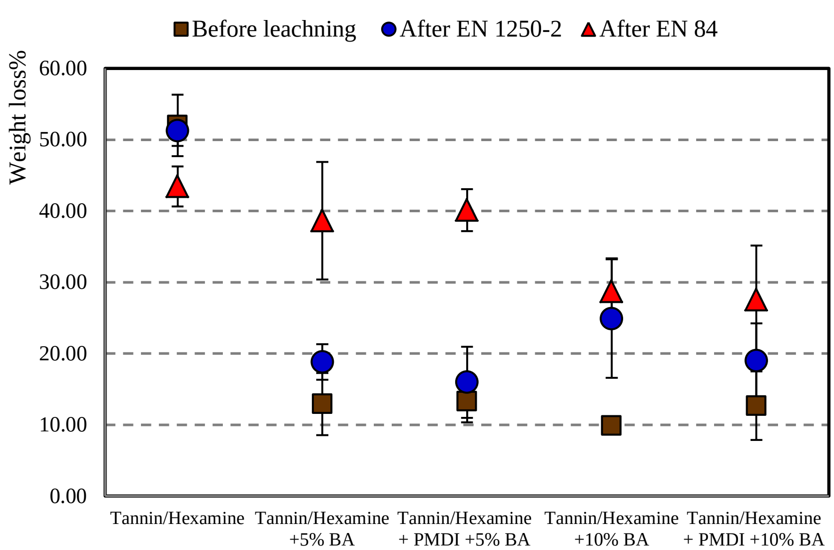


Figure 7.8 Average weight loss of beech plywoods with treated glue line before and after leaching, at 50% tannin concentration. Attack by the white rot fungus *Trametes versicolor*.

7.1.3 Plywood samples made with treated veneers

The plywoods made with treated veneers were considered to bond class 2 applications. In this service conditions the moisture content can occasionally increase to a level which can allow the growth of wood-destroying fungi (use class 2 or even use class 3.1). Risk of insect attack is depended to geographical region (EN 335, 2013).

7.1.3.1 Beech plywood

7.1.3.1.1 Before leaching

The results of fungal test before leaching for beech plywoods made of treated veneers are presented in Figure 7.9. The control plywood samples and plywoods made of water treated veneers did not show any resistance against fungus and their weight loss was as much as beech size controls (Table 7.1).

The result of humidity at the end of the test (Annex D; Table D. 7) showed that humidity of control plywoods was lower than beech size controls. It means that MUF gluelines can decrease uptake of moisture and play a role like a barrier against water. The plywoods made with treated veneers had the lower humidity than control plywoods. The weight losses for plywoods with treated veneers were below 3% (with the exception of plywoods made from treated veneers with 10% tannin-0.5% BA when core layer was left untreated). Based on the ENV 12038 (2003) the humidity at the end of the test should be above 20% to confirm the validity of the test when weight loss is below 3%. In this study the humidity for treatments with weight losses below 3% were above 30%, thus the test is valid.

The plywoods made of treated veneers with 0.5% BA alone solution and even with untreated core layer showed considerable resistance against the fungal attack. The samples made of treated veneers with 10% tannin- 0.5% BA resulted in a bit more weight loss compared to the BA alone solutions particularly when core layer was left untreated. The possible explanations for this could be the lower retention of BA in the tannin-boron solutions than BA alone solution (Table 5.3). On the other hand, the growth of fungus is inhibited when fungus attacks to a fully treated ply first, and the resistance comes mainly from that.

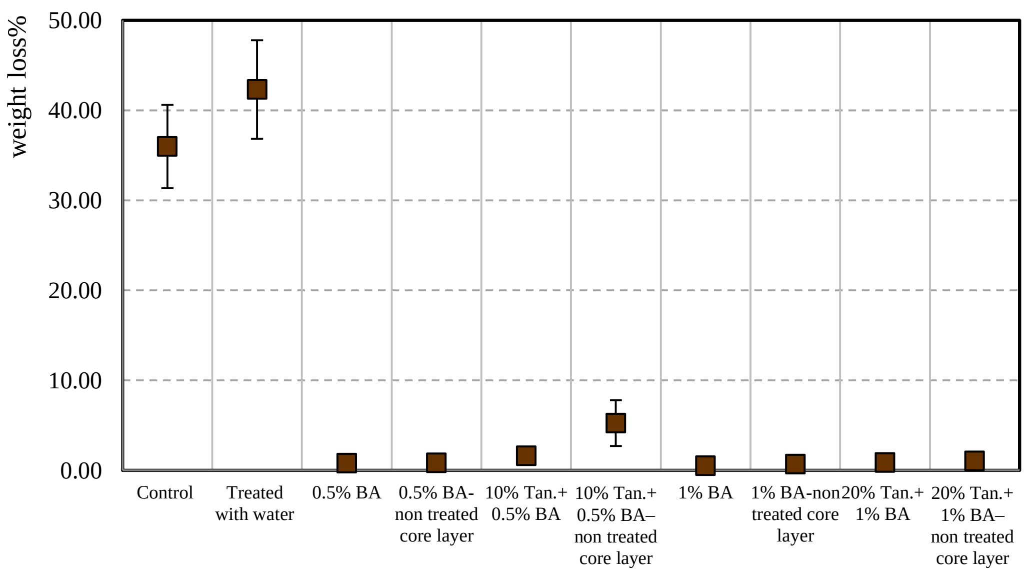


Figure 7.9 Average weight loss of beech plywoods made with treated veneers before leaching. Attack by the white rot fungus *Trametes versicolor*

The minimum retention of BA (Table 5.3) and the maximum weight loss was related to the plywoods made of treated veneers with 10% tannin- 0.5% BA when core layer was left untreated. The weight losses of plywood samples made of treated veneers with 1% BA either alone or associated with tannin were below 1%. The results of ANOVA and Duncan test for the weight loss values are summarized in Table C. 49 and C.50 (Annex C.2).

7.1.3.1.2 **After EN 1250-2**

The results of fungal test after EN 1250-2 leaching procedure are presented in Figure 7.10. The weight loss of the control plywoods and samples made of treated veneers with water were approximately as much as before leaching values.

The humidity at the end of the test for plywood samples made with BA alone solution and non-treated core layer were approximately as much as control plywoods (above 100%) (Annex D; Table D.8). The rest of treatments had lower humidity particularly in 20% tannin- 1% BA (54%). The weight losses of plywood panels made of treated veneers with BA alone solutions (0.5% or 1% BA) were considerably increased after leaching process when core layer was left untreated (approximately 40% weight loss). Duncan test grouped these treatments in a same subset along with the control treatments (Annex C.2; Tables C.51 and C.52). This means that all the boron was removed during leaching procedure. The plywood samples treated with BA alone solutions when all layers were treated showed still partially resistant against fungal attack (below 30% weight loss). A possible explanation for this can be the effect of MUF bond line on the hydrophobicity and boron diffusion in the plywood configurations. In fact MUF play a role like a barrier against boron diffusion from core layer.

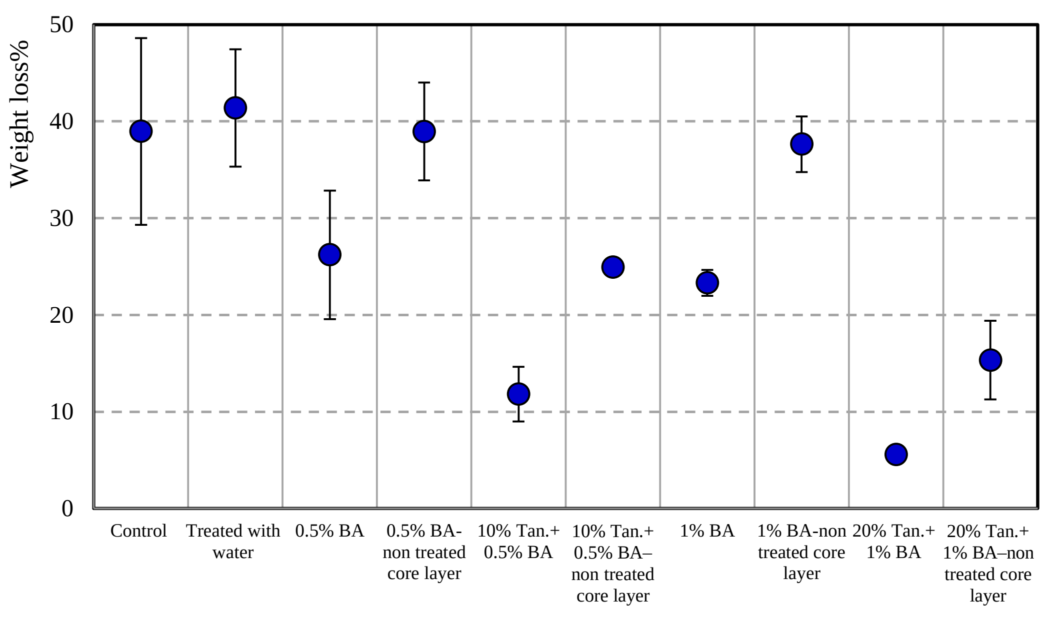


Figure 7.10 Average weight loss of beech plywoods made with treated veneers after EN 1250-2. Attack by the white rot fungus *Trametes versicolor*

The leached samples made of treated veneers with tannin-boron solutions present a higher weight loss values than the non-leached ones. It could be presumably due to the presence of some free BA that did not take place in the reactions of tannin resinification (Tondi et al., 2012a). The leachate waters of the initial leaching periods were brownish which can be due to the dissolution of low-molecular weight tannin oligomers. The most promising result is that the weight loss of samples made of treated veneers with 20% tannin- 1% BA was still very low (5.59 %) after leaching procedure.

7.1.3.1.3 **After EN 84**

Figure 7.11 shows the results of fungal test after EN 84 leaching test. It can be seen that the weight loss of the samples made of treated veneers with BA alone solutions (either all layers treated or non-treated core layer) are as much as untreated controls. These treatments were grouped in a same subset along with control treatment using Duncan test (Annex C.2; Table C. 53 and C.54). Also the leached samples made of treated veneers with tannin-boron solutions present a higher weight loss values than the either non-leached ones or leached according to EN 1250-2, particularly when core layer was left untreated. The weight loss of plywoods made of treated veneers with 10% tannin- 0.5% BA and non-treated core layer was as much as control plywoods. But the results obtained with 20% tannin- 1% BA were still striking especially when all layers were treated.

The results of humidity at end of the test are summarized in Table D.9 (Annex D). The humidity of plywood samples made of treated veneers with tannin-boron solutions (below 100%) are still lower than control and BA alone solutions (above 150%) with exceptions of 10% tannin- 0.5% BA when core layer was left untreated (125%).

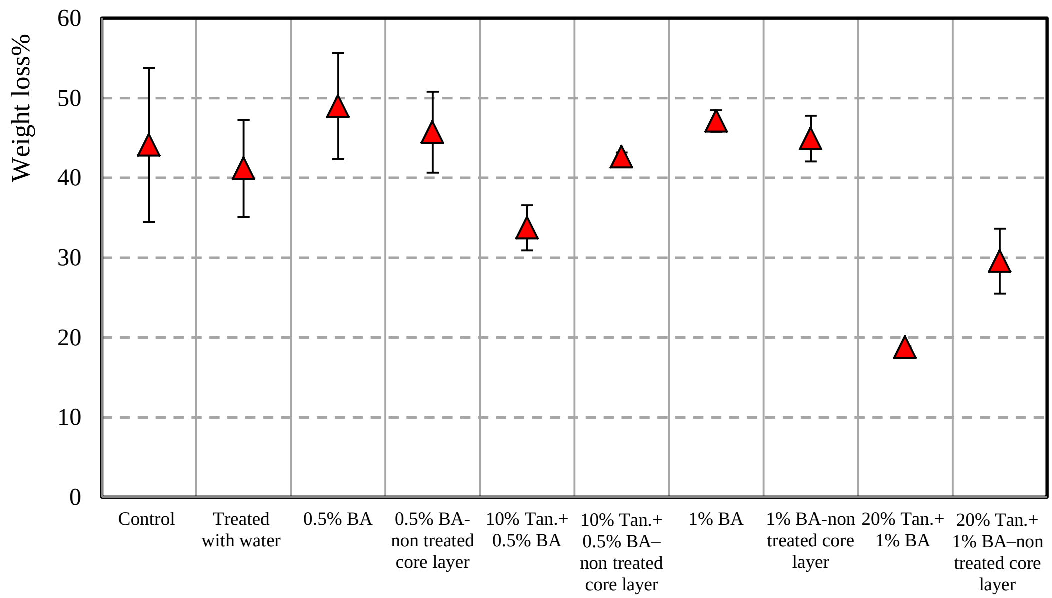


Figure 7.11 Average weight loss of beech plywoods made with treated veneers after EN 84. Attack by the white rot fungus *Trametes versicolor*

It is apparent from this result that tannin-boron system is effective in reducing boron leaching from treated wood even after strictest leaching test (EN 84). The solution with higher concentration of BA and tannin could lead to more positive outcomes in the boron fixing (Tondi et al., 2012a). But it should taken into the account that this system can cause the negative effect on the bonding quality (Figure 6.19) when more preservative solution is penetrated into the wood layers.

7.1.3.2 **Poplar plywood**

The results of fungal test before and after different leaching tests for poplar plywoods made of treated veneers are presented in Figure 7.12. The control plywood samples and plywoods made of water treated veneers did not show any resistance against fungus and their weight loss was as much as size controls of poplar wood (above 40%).

Similar to the beech plywoods, the plywoods made of treated veneers with 1% BA alone solution showed significant resistance against fungal attack before leaching (below 1% weight loss). Also the samples made of treated veneers with tannin-boron solutions even with non treated core layer presented below 1% weight losses. Duncan test grouped these treatments in the same subset (Annex C.2; Tables C. 55 and C.56). The humidity of control plywoods at the end of the test (Annex D; Table D.10) were approximately as much as poplar size control (above 150%), but the plywoods with treated veneers showed significantly lower humidity (around 50%). Since the humidity of the samples with below 3% weight loss was higher than 20% so the test is valid (ENV 12038).

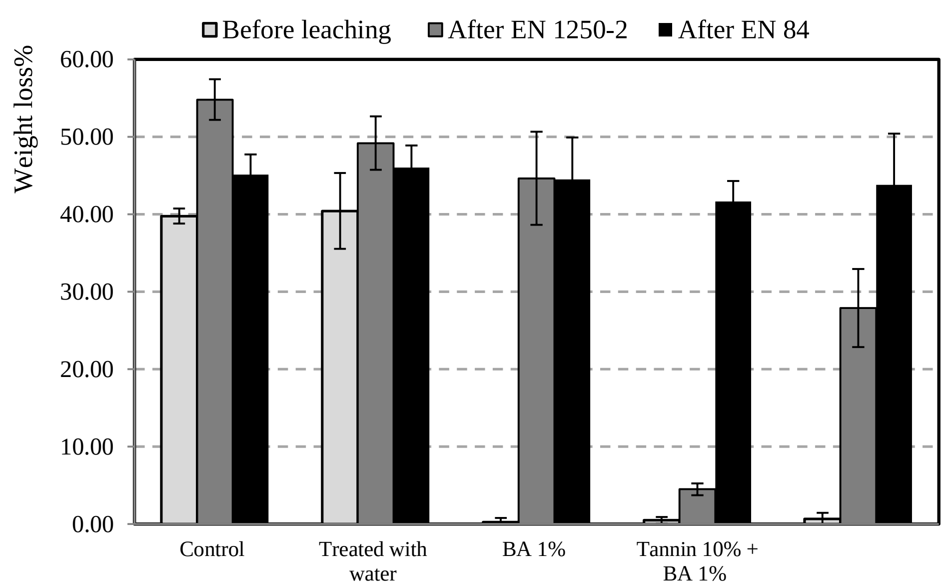


Figure 7.12 Fungal test results of poplar plywoods made of treated veneers before and after leaching tests. Attack by the white rot fungus *Trametes versicolor*

After EN 1250-2 (1995), the weight loss of samples made of treated veneers with BA alone solution were drastically increased (above 40%). It seems that all the boron was leached out. Duncan test grouped this treatment in one subset along with controls (Annex C.2; Tables C. 55

and C. 56). Also the samples made of treated veneers with tannin-boron solutions present a higher weight loss values than the non-leached ones, but still showed significant resistance against fungal attack, particularly when all layers were treated (4.5% weight loss). The results of humidity at the end of test are summarized in Table D.10 (Annex D). The plywood samples made from treated veneers with 10% tannin- 1% BA significantly showed lower humidity than control plywoods or plywoods treated with BA alone solution.

The result of fungal test after EN 84 (1997) was not satisfactory. The weight loss of plywoods made of treated veneers with tannin-boron system was as much as control plywoods. No statistically difference was observed between treatments (Annex C.2; Table C. 55). The beech plywoods, also, made with treated veneers with same tannin concentration did not bring any improvement after EN 84. This is may be because of low degree of polymerization of tannins with only 10% tannin in the solution. Previous study on the tannin-boron solution on the pine and beech solid wood (Tondi et al., 2012a) revealed that satisfactory results can obtained with a strong polymeric network (20% of tannin in the formulation).

7.1.4 Conclusions for the fungal test

The following conclusions can be drawn from the fungal test on beech and poplar plywoods with treated gluelines or treated veneers:

1. The addition of borate into the tannin glue provided effective resistance against fungal attack even after mild leaching test according to the EN 1250-2 (1995). EN 84 (1997) leaching tests caused drastic increase in the weight loss of plywood samples. It looks that all the boron was leached out by this leaching procedure.
2. The addition of 4% BA to the quebracheo tannin adhesive at 50% tannin concentration caused the lower weight loss in poplar plywoods compared to the addition of 10% BA into the mimosa tannin adhesive in the beech plywoods. It can be concluded that toxic threshold of BA is highly depended to the wood species and density.
3. However the plywood samples made of treated veneers with BA alone solution showed good resistance against fungal attack. But their effectiveness was lost even after mild leaching test (EN 1250-2). They showed significant sensitivity against biological deterioration after leaching test like control samples.
4. The plywoods made of treated veneers with tannin-boron solutions showed high resistance against fungal attack even after EN 1250-2 and to some extent after EN 84 depending on the concentration of tannin and BA in the solutions. The satisfactory results were obtained with a strong polymeric network of tannin (20% tannin in the formulation). The plywoods with untreated core layer showed lower resistance against fungal attack particularly after leaching tests.

7.2 Termite tests

7.2.1 Solid wood control

Tables 7.2 and 7.3 give the results of termite test for solid wood of beech and poplar according to the EN 117 (2013) and EN 118 (2014) respectively. The attack of pine sapwood in both standard methods clearly showed that termites were active under the test conditions: more than 50% survival rate and level 4 of degree of attack. Thus the tests are valid.

Beech and poplar wood (standard dimensions or size controls) were corresponded to level 4 of attack in both standards methods. But poplar wood showed higher weight loss and survival rate than the beech wood. The weight loss and survival rate of size control samples were more than controls with standard size.

Table 7.2 Results of termite test according to the EN 117 for the solid wood of beech and poplar. Attack by the European termite *Reticulitermes flavipes* (*ex. santonensis*).

Type of sample	Weight loss %	Survival rate %	Visual rating rank
Virulence controls of pine sapwood ($50 \times 25 \times 15$ mm^3)	8.77 (1.72)	62.00 (10.35)	4
Controls of poplar wood ($50 \times 25 \times 15$ mm^3)	9.54 (2.34)	44.13 (9.25)	4
Size controls of poplar wood ($50 \times 25 \times 6$ mm^3)	24.20 (4.37)	48.4 (11.78)	4
Controls of beech wood ($50 \times 25 \times 15$ mm^3)	4.93 (0.45)	39.07 (1.97)	4
Size controls of beech wood ($50 \times 25 \times 6$ mm^3)	20.64 (1.95)	62.80 (8.40)	4

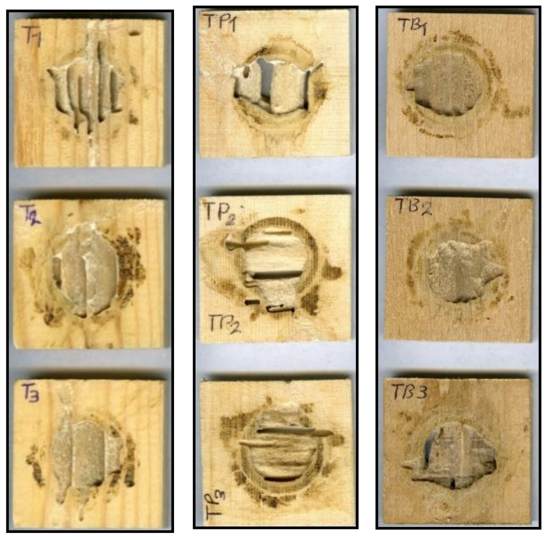
Table 7.3 Results of termite test according to the EN 118 for the solid wood of beech and poplar. Attack by the European termite *Reticulitermes flavipes* (*ex. santonensis*)

Type of sample	Survival rate % (Std. dev.)	Visual rating rank
Virulence controls of pine sapwood ($50 \times 50 \times 15$ mm^3)	65.47 (6.65)	4
Size controls of poplar wood ($50 \times 50 \times 6$ mm^3)	60.20 (1.41)	4
Size controls of beech wood ($50 \times 25 \times 6$ mm^3)	48.60 (8.20)	4

Figure 7.13 illustrates some test samples after EN 117 (2013). Similar to the virulence controls, poplar and beech controls underwent level 4 of attack. This shows that the wood of beech and poplar are very susceptible to termite damage. Termites consumed the earlywood with the higher rate than the latewood and caused sheet structures. Figure 7.14 exhibits some test samples after EN 118 (2014). All the samples underwent level 4 of degree of attack. Termites had eaten the samples in the thickness direction until the other side through annual rings.

From left to right: pine sapwood, poplar size controls, and beech size controls.

Figure 7.13 Some test specimens after EN 117 for virulence and control samples



From left to right: pine sapwood, poplar size controls, and beech size controls.

Figure 7.14 Some test specimens after EN 118 for virulence and control samples

7.2.2 Plywood samples with treated glue line

7.2.2.1 **Poplar plywood**

7.2.2.1.1 **EN 117**

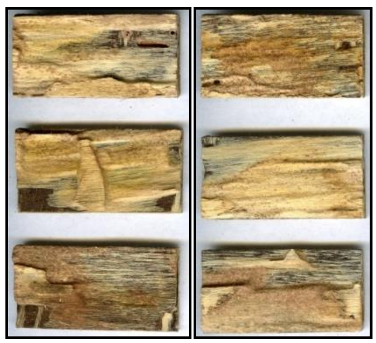
The results of EN 117 for poplar plywoods with treated gluelines (Table 7.4) showed that the amount of BA loading into the glueline was not adequate to provide full protection against termite attack. All the samples were attacked strongly by termites and underwent level 4 of degree of attack similar to the control plywoods (without BA). No effect was observed by PMDI addition. Increase in the BA content of the adhesive up to 4% caused lower survival rate and weight loss than controls but visual rating showed no difference between treatments.

The weight loss values for poplar plywoods were more than poplar size controls (above 25%) with the exception of formulation containing 4% BA in the glue. Termites had eaten plywood samples with a greater craving.

Some test samples after EN 117 are shown in Figure 7. 15. Most of the time gluelines have been perforated by termites (not eaten). They attacked to the core layer through the glue line after chewing surface layers.

Table 7.4 Results of termite test according to the EN 117 for the poplar plywoods with treated glue at 50% tannin concentration. Attack by the European termite *Reticulitermes flavipes* (*ex. santonensis*)

Formulations	Weight loss (Std. dev.) %	Survival rate (Std. dev.) %	Visual rating rank
Tannin/Hexamine	27.78 (5.46)	60.93 (6.11)	4
Tannin/Hexamine + PMDI	33.08 (3.66)	54.13 (2.01)	4
Tannin/Hexamine + PMDI + BA 2%	33.26 (8.20)	50.27 (5.60)	4
Tannin/Hexamine + PMDI + BA 3%	27.65 (2.89)	43.60 (9.41)	4
Tannin/Hexamine + PMDI + BA 4%	21.64 (1.30)	25.20 (21.90)	4



From left to right: 50% tannin/hexamine- PMDI, 50% tannin/hexamine- PMDI- 4% BA.

Figure 7.15 Some test specimens after EN 117 for poplar plywoods made with tannin glue.

7.2.2.1.2 EN 118

No notable differences were found between the results of EN 117 and EN 118. All the samples were strongly attacked by termites and underwent level 4 of degree of attack (Table 7.5).

Table 7.5 Results of termite test according to the EN 118 for the poplar plywoods with treated glue at 50% tannin concentration. Attack by the European termite *Reticulitermes flavipes* (*ex. santonensis*)

Formulations	Survival rate (Std. dev.) %	Visual rating rank
Tannin/Hexamine	71.47 (4.55)	4
Tannin/Hexamine+ PMDI	67.47 (2.44)	4
Tannin/Hexamine+ PMDI+ BA 2%	64.67 (4.84)	4
Tannin/Hexamine+ PMDI+ BA 3%	52.40 (3.12)	4
Tannin/Hexamine+ PMDI+ BA 4%	34.67 (15.83)	4

Similar to the EN 117, increase in the BA content of the glue up to 4% only caused less survival rate. The lowest survival rate was recorded for the plywoods made of adhesive containing 4% BA.
Figure 7.16 renders some test samples after EN 118 (2014). As can be seen, the including BA gluelines are Intact, but perforated by termites. After chewing the surface layer, termites made holes through the gluelines to get access to the lower layers.

From left to right: 50% tannin/hexamine- PMDI, 50% tannin/hexamine- PMDI- 4% BA.

Figure 7.16 Some test specimens after EN 118 for poplar plywoods made with tannin glue

Borate is very toxic to termites even at 0.24% w/w BAE and causes significant mortality (Ahmed et al., 2004). But commercial retentions recommended for protection against termites for solid wood are usually in excess of 1% BAE equal to 4.5 kg/m^3 depending on wood density (Schoeman & Lloyd, 1998). The maximum uptake and retention of BA which was loaded in the gluelines of this set of plywood was 0.2% w/w and 0.811 kg/m^3 respectively. Borates are not repellent for insects. Once ingested, borates serve as a slow-acting stomach poison (Lloyd et al., 1998). Therefore a little bit of the treated wood can be eaten by termites even at high retention of borates.
This set of plywoods showed low performance against termites. Therefore current standards (EN 117 and EN 118) were not carried out on the leached samples. The leached samples as well as not leached ones were used in the choice feeding tests. In this test, three samples were introduced into the each container at the same time.

7.2.2.1.3 **Choice feeding test**

The results of choice tests for this set of plywoods are shown in Table 7.6. The attack of pine sapwood with one sample or three samples in each container clearly showed that (1) termites were active under the test conditions and (2) there was enough pressure on the samples from the termites (more than 50% survival rate and level 4 of attack). The average of weight loss was lower when three virulence controls were introduced in each container.

Table 7.6 Results of choice termite tests for the poplar plywoods at 50% tannin concentration

Formulations		Weight loss (Std. dev.) %	Survival rate (Std. dev.) %	Visual rating rank
Virulence controls of pine sapwood		12.51 (0.29)	51.00 (6.01)	4
Virulence controls of pine sapwood With three samples	**1)** Pine sapwood	8.01 (2.32)	56.23 (4.21)	4
	2) Pine sapwood			4
	3) Pine sapwood			4
Control plywoods without BA	**1)**Tannin/Hexamine+PMDI	15.88 (4.28)	55.33 (4.28)	4
	2)Tannin/Hexamine+PMDI			4
	3)Tannin/Hexamine+PMDI			4
Before leaching	**1)**Tannin/Hexamine+PMDI	17.96 (5.45)	35.07 (5.60)	4
	2)Tannin/Hexamine+PMDI+BA 2%	16.85 (5.96)		4
	3)Tannin/Hexamine+PMDI+BA 4%	14.61 (2.94)		4
After EN 1250-2	**1)**Tannin/Hexamine+PMDI	16.27 (4.10)	44.00 (5.60)	4
	2)Tannin/Hexamine+PMDI+BA 2%	18.93 (4.08)		4
	3)Tannin/Hexamine+PMDI+BA 4%	15.23 (5.18)		4
After EN 84	**1)**Tannin/Hexamine+PMDI	15.61 (3.43)	53.32 (4.34)	4
	2)Tannin/Hexamine+PMDI+BA 2%	14.65 (1.21)		4
	3)Tannin/Hexamine+PMDI+BA 4%	16.56 (4.02)		4

For the control test, three without BA plywoods were introduced in each container. For the main test, one control plywood (without BA) and two BA containing ones (different concentration) were put in each container. All plywoods were attacked strongly by termites and underwent level 4 of degree of attack. No difference was observed in the results of visual examinations between treatments. The only major result was a few reductions in the survival rate before leaching when BA including plywoods were present in the container. Also BA including samples showed lower weight loss before leaching. After leaching (particularly EN 84) survival rate was as much as control tests. No trend in weight loss was observed after leaching tests.

7.2.2.2 **Beech plywood**

7.2.2.2.1 **EN 117**

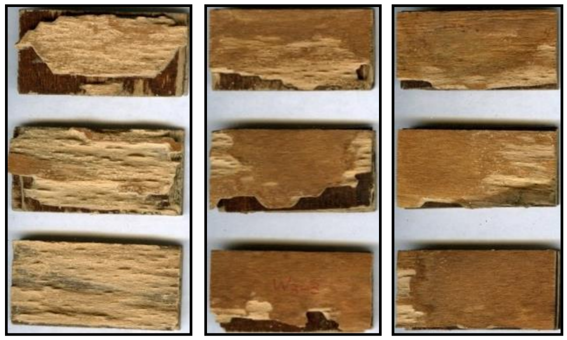
Table 7.7 presents the result of termite tests according to the EN 117 (2013) for the beech plywoods at 45 and 50% tannin concentration. The results showed that survival rate was reduced following the addition of BA to the glue. No living termite was found associated to the 10% BA in the adhesive (with or without PMDI). Also, the plywoods underwent lower degree of attack following the addition of BA. The adding BA and increase in its content from 5 to 10 % decreased the percentage of weight loss. However, all termites died in association with 10% BA in the glueline but these treatments are not effective treatment according to EN117 (2013). Based on this standard to be an effective treatment, (1) the survival rate must be 0% and (2) the level of attack should be 0 or 1 (or maximum level 2 in two samples out of five). But in these treatments the levels of attack are 2 or 3. This can be related to the non repellent characteristic of borates against insects. Termites eat some of the sample before dying. So, here, the survival rate is 0% but there is degradation on the plywood samples. On the other hand, this amount of BA loading in the glue markedly reduced bonding quality (Figure 6.13). The treatments with 5% BA, also, caused significant termite mortality, less weight loss, and lower rank of attack compared to the controls.

Table 7.7 Results of termite test according to the EN 117 for the beech plywoods with treated glues. Attack by the European termite *Reticulitermes flavipes* (*ex. santonensis*)

Formulations	Weight loss % (Std. dev.)	Survival rate % (Std. dev.)	Visual rating rank
Virulence controls of pine sapwood	13.73 (0.54)	60.93 3.11	4
45% tannin concentrations			
Tannin/Hexamine	17.18 (1.89)	47.33 (7.66)	4
Tannin/Hexamine + 5% BA	10.74 (0.43)	8.93 (7.80)	3, 3, 4*
Tannin/Hexamine + PMDI + 5% BA	12.17 (1.94)	15.07 (15.63)	4, 4, 3
Tannin/Hexamine + 10% BA	4.48 (1.22)	0 0	2, 2, 2
Tannin/Hexamine + PMDI + 10% BA	5.06 (2.13)	0 0	3, 3, 3
50% tannin concentrations			
Tannin/Hexamine	19.47 (1.05)	51.87 (2.31)	4
Tannin/Hexamine + 5% BA	10.85 (1.69)	4.80 (8.31)	4, 4, 3
Tannin/Hexamine + PMDI + 5% BA	11.71 (1.96)	6.67 (6.60)	4, 3, 3
Tannin/Hexamine + 10% BA	3.52 (1.22)	0 0	3, 3, 2
Tannin/Hexamine + PMDI + 10% BA	5.21 (2.02)	0 0	3, 3, 2

* Result of visual rating for the different samples when they are not same.

Figure 7.17 presents some test samples for beech plywood after EN 117. Similar to the poplar plywoods, BA containing glueline was left intact. The surface layers were only chewed by termites. Compare to the poplar plywoods (Figure 7.15), the extent of damage was lower for beech plywoods even in the control formulation (without BA). Poplar control plywoods rendered higher weight loss (and survival rate).



From left to right: 50% tannin/hexamine, 50% tannin/hexamine+5% BA, and 50%tannin/hexamine+10% BA.

Figure 7.17 Some test specimens after EN 117 for beech plywoods made with tannin glue

7.2.2.2.2 **EN 118**

The results obtained for the termites test according to the EN 118 (2014) are presented in Table 7.8 for beech plywoods at 45 and 50% tannin concentration.

The results of EN 117 and EN 118 were largely close together. The survival rates were reduced following the addition of BA. No living termite was found associated to the 10% BA including adhesive (without PMDI). In general, the numbers of survivor termites were higher than EN 117.

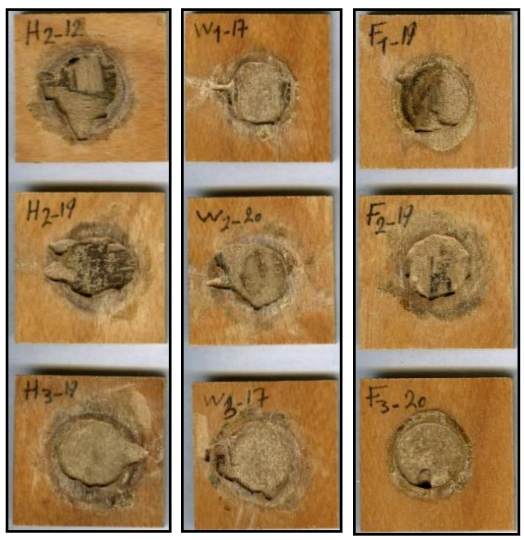
Table 7.8 Results of termite test according to the EN 118 for the beech plywoods with treated glue. Attack by the European termite *Reticulitermes flavipes* (*ex. santonensis*)

Treatment	Survival rate % (Std. dev.)	Visual rating rank
Virulence controls of pine sapwood	64.66 (7.82)	4
45% tannin concentrations		
Tannin/Hexamine	58.27 (5.66)	4
Tannin/Hexamine + 5% BA	24.13 (4.03)	4
Tannin/Hexamine + PMDI + 5% BA	32.40 10.05	4
Tannin/Hexamine + 10% BA	0 0	4
Tannin/Hexamine + PMDI + 10% BA	6.27 (10.85)	4
50% tannin concentrations		
Tannin/Hexamine	56.27 (12.61)	4
Tannin/Hexamine + 5% BA	21.20 (12.26)	4
Tannin/Hexamine + PMDI + 5% BA	13.73 11.90	4
Tannin/Hexamine + 10% BA	0 0	4
Tannin/Hexamine + PMDI + 10% BA	5.20 9.01	4

All the samples underwent level 4 of attack. In EN 118, termites are in contact with a small area of the specimens. Because of this difference in the area exposed to the termites, the degree of attack was more homogeneous and strong than with EN 117. On the other hand, the BA was only used in the glue line, whereas the surface of plywoods was exposed to the termites. But borates can utilize the natural moisture in the wood to diffuse deeper over time, especially in wood having a humidity of greater than or equal to 15 % (Lloyd et al., 1998). Therefore, BA diffusion was possible during the test time.

Figure 7.18 illustrate some test samples after EN 118 for beech plywoods with treated glueline. Despite the deference in the extent of damage but according to the standard guidelines in EN 118 (2014) all the samples underwent level 4 of attack. In the control without BA plywoods the glueline was mainly attacked by termites. But in BA containing plywoods, the most of the time glueline was intact or perforated by termites to get access to the lower layers.

Similar to the poplar plywoods, EN 117 (2013) and EN 118 (2014) were not carried out on the leached beech plywoods with treated glue line. Instead choice feeding tests were done on the leached as well as not leached samples.



From left to right: 50% tannin/hexamine, 50% tannin/hexamine+5% BA, and 50%tannin/hexamine+10% BA.

Figure 7.18 Some test specimens after EN 118 for beech plywoods made with tannin glue

7.2.2.2.3 **Choice feeding test**

The results of choice tests for this set of plywoods are shown in Table 7.9. The test was done only on treatments that had the best performance, regarding to pervious the termite tests and bonding quality. For example the choice feeding test was not done on the samples including 10% BA in the glueline, because these plywoods did not meet standard requirements for bond class 1 (Figure 6.13).

The attack of control plywoods with three samples in each container clearly showed that there was enough pressure on the samples from the termites (high weight loss and level 4 of attack). No difference was observed in the results of visual examinations after EN 84 and all samples were subjected to level 4 of attack). Some samples with 5% BA in the glue line showed lower degree of attack after mild leaching test (EN 1250-2). Termites did not make a clear choice between treatments and the samples with varying amount of BA were attacked in the same manner. The weight losses were same between different samples in the same container, but lower than those obtained when three controls were in the container. The containers including samples with BA showed significant reduction in the survival rate, particularly before leaching or after mild leaching test. The borates are very toxic to termites and other insects but they are not repellent (Lloyd et al., 1998). So even in choice test all the samples were attacked by termites.

		Weight loss (Std. dev.) %	Survival rate (Std. dev.) %	Visual rating rank
Controls without BA	**1)**Tannin/Hexamine	10.55 (3.14)	46.40 (5.89)	4
	2)Tannin/Hexamine			4
	3)Tannin/Hexamine			4
Before leaching	**1)**Tannin/Hexamine	4.29 (0.32)	19.60 (18.68)	4, 4, 3*
	2)Tannin/Hexamine+BA 5%	4.03 (0.13)		4, 4, 3
	3)Tannin/Hexamine+PMDI+BA 5%	3.98 (0.14)		4, 4, 3
After EN 1250-2	**1)**Tannin/Hexamine	4.20 (0.31)	29.73 (8.73)	4, 4, 4
	2)Tannin/Hexamine+BA 5%	3.91 (0.05)		3, 3, 4
	3)Tannin/Hexamine+PMDI+BA 5%	4.00 (0.18)		4, 4, 3
After EN 84	**1)**Tannin/Hexamine	4.01 (0.30)	35.20 (0.83)	4
	2)Tannin/Hexamine+BA 5%	3.97 (0.17)		4
	3)Tannin/Hexamine+PMDI+BA 5%	4.21 (0.20)		4

*Result of visual rating for the different samples when they are not same

Table 7.9 Results of choice feeding tests for the beech plywoods at 50% tannin concentration.

7.2.3 Plywood samples made with treated veneers

7.2.3.1 **Beech plywoods**

7.2.3.1.1 **Before leaching**

7.2.3.1.1.1 **EN 117**

The results obtained from the termites tests according to the EN 117 are presented in the Table 7.10 for beech plywoods with treated veneers. Termite damages in control plywoods as well as plywoods made of treated veneers with water caused high weight loss and all samples were subjected to level 4 of degree of attack (Figure 7.19). The survival rates of these treatments were lower than those obtained for virulence controls.

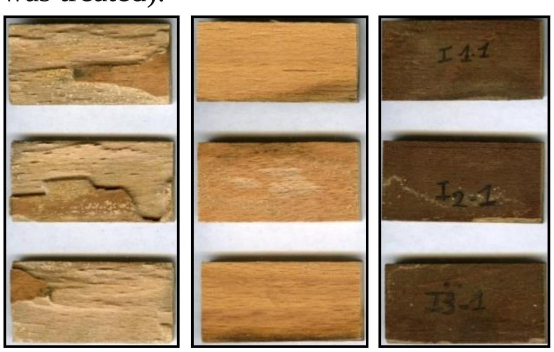
The samples made of treated veneers with BA alone solutions showed shallow testing nibbles, which were mainly on the surface (Figure 7.19) and the termites died after the attack (in the first week of exposure). The most of the plywood specimens made of treated veneers with 0.5 or 1% BA solution either treated or untreated core layer (10 out of 12) underwent level 1 of degree of attack. The percentage of weight loss was very low in these treatments. These treatments are efficient based on the criteria explained in EN 117 (2013).

Table 7. 10 Results of termite test according to the EN 117 for the beech plywoods made of treated veneers before leaching. Attack by the European termite *Reticulitermes flavipes* (*ex. santonensis*)

Tannin/Hexamine solution %	Boric acid %	Core layer + treated -untreated	Weight loss (Std. dev.) %	Survival rate (Std. dev.) %	Visual rating rank
Virulence controls of pine sapwood (50 × 25 × 15 mm3)			17.06 (1.99)	57.33 4.67	4
Control plywood			21.09 (3.01)	37.87 (3.45)	4
Treated with water			14.29 (4.02)	29.87 (4.11)	4
−	0.5	+	1.08 (0.67)	0	1,1,2*
−	0.5	−	1.56 (2.20)	0	1,1,1
10	0.5	+	5.11 (1.86)	0	2,2,2
10	0.5	−	2.41 (0.96)	0	3,3,2
−	1	+	0.71 (0.14)	0	1,0,1
−	1	−	0.54 (0.52)	0	1,1,1
20	1	+	2.86 (1.67)	0	1,1,2
20	1	−	2.65 (1.41)	0	2,1,3

* Result of visual rating for the different samples when they are not same

In the plywoods made of treated veneers with tannin-boron system a deeper area was nibbled by termites that were occurred mainly on the edges. All termites died after one or two weeks of exposure depending on the concentration of chemicals in the solutions. At the same BA concentration, termites ate treated samples with tannin-boron systems with the higher rate and caused higher percentage of weight loss as well as degree of attack than BA alone solutions. It is worth mentioning that BA retention in the tannin- boron solutions was lower than that obtained with BA alone solution at same concentration (Table 5.3). The treatment with 20% tannin- 1% BA can be specified as efficient treatment in according to standards requirements with a little tolerance (when core layer was treated).



From left to right: control, treated with 1% BA, treated with 20% tannin- 1% BA

Figure 7.19 Some test specimens after EN 117 for beech plywoods made with treated veneers before leaching.

7.2.3.1.1.2 **EN 118**

The results of termites test according to EN 118 (2014) are summarized in Table 7.11. In according to the virulence samples, the validity of test is confirmed with a little tolerance. The virulence underwent level 4 of degree of attack but the survival rate was a little lower than standard requirement (48.60 % survival rate).

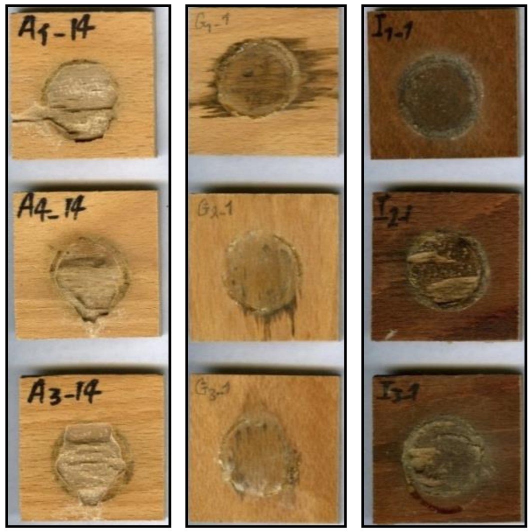
Similar to the EN 117, Termites attack in control plywoods as well as plywoods made of treated veneers with water caused level 4 of attack (Figure 7.20). In the plywood made of treated veneers with BA alone or tannin-boron system, all termites died after one or two weeks of exposure depending on the concentration of BA in the solution. The treatment with 0.5% BA (when all layers were treated) and 1% BA (even with untreated core layer) are efficient according to the criteria explained in EN 118 (2014). The rank of attack by the visual examination showed the higher level of degree of attack compared to the EN 117. This can be due to the limited surface area (around 450 mm^2) which is exposed to the termite damage in EN 118. In facts these tests are designed differently for different purpose. EN 118 is designed to determine protective effect of the surface, but EN 117 is designed to determine preventive effect of full treatment.

Table 7.11 Results of termite test according to the EN 118 for the beech plywoods made of treated veneers . Attack by the European termite *Reticulitermes flavipes* (*ex. santonensis*)

Tannin/Hexamine solution %	Boric acid %	Core layer + treated -untreated	Survival rate (Std. dev.) %	Visual rating rank
Virulence controls of pine sapwood (50 × 25 × 15 mm3)			48.60 (3.11)	4
Control plywood			37.60 (2.83)	4
Treated with water			34.60 (8.20)	4
−	0.5	+	0	2,1,1*
−	0.5	−	0	4,2,1
10	0.5	+	0	2,3,3
10	0.5	−	0	4,3,3
−	1	+	0	1,0,1
−	1	−	0	0,1,0
20	1	+	0	1,3,3
20	1	−	0	4,3,3

* Result of visual rating for the different samples when they are not same

Half of the plywood specimens made of treated veneers with 0.5 or 1% BA alone solution either treated or untreated core layer (6 out of 12) underwent level 1 of degree of attack. The most of the plywood specimens made of treated veneers with 10% tannin- 0.5% BA or 20% tannin- 1% BA solutions either treated or untreated core layer (8 out of 12) underwent level 3 of degree of attack (Table 7.11 and Figure 7.20).



From left to right: control, treated with 1% BA, treated with 20% tannin- 1% BA

Figure 7.20 Some test specimens after EN 118 for beech plywoods made with treated veneers before leaching

7.2.3.1.1.3 **Choice feeding test**

The results of choice tests before leaching are presented in Table 7.12. The degree of attack in control plywoods with three samples in each container clearly showed that there was enough pressure on the samples from the termites (high weight loss and level 4 of attack). However, the weight loss is lower than that obtained by EN 117 when there was single sample in the container (Table 7.10).

Table 7.12 Results of choice feeding tests for the beech plywood made of treated veneers before leaching

	Weight loss (Std. dev.) %	Survival rate (Std. dev.) %	Visual rating rank
Virulence controls of pine sapwood	14.47 (2.11)	56.93 (6.28)	4
1) Control plywood	9.78 (1.61)	53.07 (3.03)	4
2) Control plywood			4
3) Control plywood			4
1) Control plywood	2.04 (0.76)	0	2, 2, 1*
2) 0.5% BA	0.65 (0.29)		1, 1, 1
3) 1% BA	0.56 (0.34)		1, 1, 0
1) Control plywood	5.55 (1.88)	0	3, 3, 4
2) 0.5% BA- untreated core	1.10 (1.24)		1, 1, 2
3) 1% BA- untreated core	0.96 (0.19)		2, 2, 0
1) Control plywood	13.07 (0.77)	18.13 (3.61)	4, 4, 4
2) 10% Tannin + 0.5% BA	3.06 (0.57)		2, 2, 0
3) 20% Tannin + 1% BA	3.22 (0.78)		3, 2, 0
1) Control plywood	8.97 (2.59)	25.20 (1.06)	4, 4, 4
2) 10% Tannin + 0.5% BA- untreated core	6.19 (0.82)		3, 3, 4
3) 20% Tannin + 1% BA- untreated core	3.86 (0.62)		2, 2, 2

* Result of visual rating for the different samples when they are not same

As can be seen, all termites died at the end of the test when alternative samples were treated with BA alone solutions. But termites made a clear choice, when alternative samples were treated with tannin-boron systems. The control plywoods were attack faster and caused higher weight loss and underwent level 4 of attack. Some number of termites was still living at the end of the test. The amount of weight loss in control samples was considerable and as much as or greater than when there were three controls in the container. Since borates are not repellent to insects (Lloyd et al., 1998) these results was very surprising. The lower degree of attack was related to the higher BA and tannin concentration.

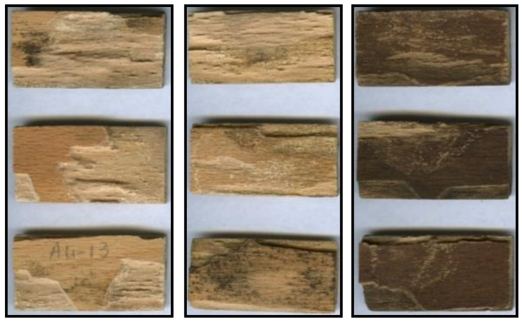
7.2.3.1.2 **After EN 1250**

7.2.3.1.2.1 **EN 117**

The results of termites test according EN 117 after EN 1250-2 leaching test are presented in Table 7.13. The plywood samples made of treated veneers with BA alone solutions lost their effectiveness against termites attack after EN 1250-2. But plywood samples made of treated veneers with tannin-boron systems still caused significant mortality and the lower weight loss. No difference was detected between the results of visual examination between the treatments and all samples underwent level 4 of attack (Figure 7.21).

Table 7.13 Results of termite test according to the EN 117 for the beech plywoods made of treated veneers after EN 1250-2. Attack by the subterranean termite *Reticulitermes flavipes* (*ex. santonensis*)

Tannin/Hexamine solution %	Boric acid %	Core layer + treated -untreated	Weight loss (Std. dev.) %	Survival rate (Std. dev.) %	Visual rating rank
Virulence controls of pine sapwood			12.87 (1.58)	59.60 (3.46)	4
Control plywood			15.22 (2.72)	47.60 (4.23)	4
–	0.5	+	13.97 (1.70)	38.67 (2.72)	4
–	0.5	–	15.53 (6.32)	41.20 (2.08)	4
10	0.5	+	11.40 (1.44)	24.40 (3.82)	4
10	0.5	–	10.82 (2.18)	25.73 (9.27)	4
–	1	+	10.51 (2.86)	39.60 (2.02)	4
–	1	–	12.68 (2.23)	41.60 (5.41)	4
20	1	+	7.07 (1.72)	0	4
20	1	–	9.01 (0.99)	14.93 (4.24)	4



From left to right: control, treated with 1% BA, treated with 20% tannin- 1% BA

Figure 7.21 Some test specimens after EN 117 for beech plywoods made with treated veneers leached by EN 1250-2

7.2.3.1.2.2 **EN 118**

Table 7.14 shows the results of termites test according EN 118 after EN 1250-2 leaching test. Unfortunately, we can see that despite a considerable amount of damage but all termites were abnormally died at the end of the tests. No survivor termites were found at the end of the test for virulence controls of pine sapwood, thus this test is not valid.

Table 7.14 Results of termite test according to the EN 118 for the beech plywoods made of treated veneers after EN 1250-2. Attack by the subterranean termite *Reticulitermes flavipes* (*ex. santonensis*)

Tannin/Hexamine solution %	Boric acid %	Core layer + treated -untreated	Survival rate %	Visual rating rank
Virulence controls of pine sapwood (50 × 25 × 15 mm3)			0	4
Control plywood			0	4
−	0.5	+	0	1,1,3*
−	0.5	−	0	1,1,3
10	0.5	+	0	1,1,3
10	0.5	−	0	4
−	1	+	0	3
−	1	−	0	4
20	1	+	0	3,4,4
20	1	−	0	4

* Result of visual rating for the different samples when they are not same

7.2.3.1.2.3 **Choice feeding test**

The results of choice feeding test are presented in Table 7.15. The alternative samples treated with BA alone solutions underwent level 4 of attack like the control plywoods. The survival rate was higher when alternative samples were treated with BA alone solutions. The containers including samples treated with tannin-boron system presented more survivors at the end of the test. The weight loss of samples treated with BA alone solutions was approximately as much as control.

Termites again made a choice when alternative samples were treated with tannin-boron systems. Control samples were attacked faster and showed higher weight loss. The plywoods treated with

20% tannin- 1% BA (all layers treated) were subjected to level 3 or 2 of attack which was lower than result obtained by EN 117 test after EN 1250-2 (Table 7.13).

Table 7.15 Results of choice termite tests for beech plywood made of treated veneers after EN 1250-2

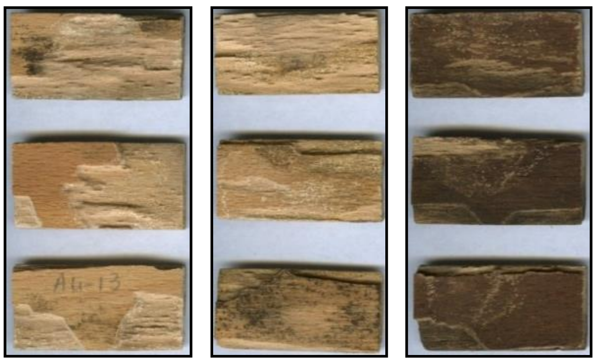
	Weight loss (Std. dev.) %	Survival rate (Std. dev.) %	Visual rating rank
1) Control plywood	9.19 (0.97)	39.60 (8.27)	4
2) 0.5% BA	7.57 (0.85)		4
3) 1% BA	7.93 (0.70)		4
1) Control plywood	9.98 (1.31)	40.13 (3.03)	4
2) 0.5% BA- untreated core	8.13 (1.20)		4
3) 1% BA- untreated core	7.76 (0.79)		4
1) Control plywood	9.37 (3.41)	30.27 (8.62)	4
2) 10% Tannin + 0.5% BA	4.83 (0.57)		4, 4, 3*
3) 20% Tannin + 1% BA	4.58 (2.63)		3, 3, 2
1) Control plywood	7.26 (1.20)	37.07 (5.69)	4
2) 10% Tannin + 0.5% BA- untreated core	7.23 (1.33)		4, 4, 3
3) 20% Tannin + 1% BA- untreated core	4.01 (1.01)		3, 3, 4

* Result of visual rating for the different samples when they are not same

7.2.3.1.3 **After EN 84**

7.2.3.1.3.1 **EN 117**

Table 7.16 presents the results of termite test according to the EN 117 (2013) after EN 84 (1997) leaching test. The plywoods made of treated veneers with BA alone solutions or tannin-boron systems showed high weight loss approximately as much as control plywoods. The rank of attack by the visual examination was level 4 for all treated and untreated plywoods (Figure 7.22). The single results obtained by tannin-boron systems was reduction in the survival rate compared to the BA alone solutions. It looks that the high amount of BA was leached out during EN 84 and the rest of BA is not sufficient to provide full protection against termite damage.



From left to right: control, treated with 1% BA, treated with 20% tannin- 1% BA.

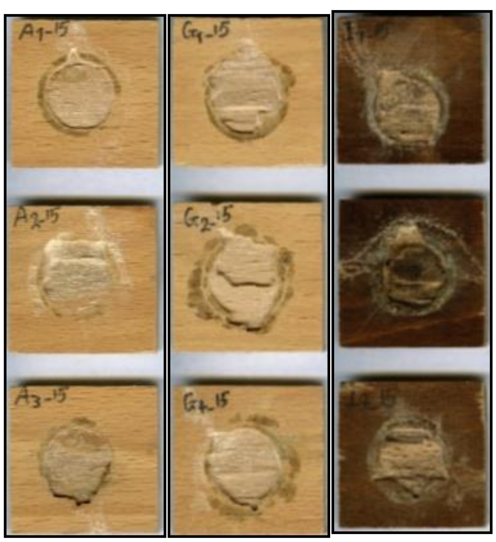
Figure 7.22 Some test specimens after EN 117 for beech plywoods made with treated veneers leached by EN 84

Table 7.16 Results of termite test according to the EN 117 for the beech plywoods made of treated veneers after EN 84. Attack by the subterranean termite *Reticulitermes flavipes* (*ex. santonensis*)

Tannin/Hexamine solution %	Boric acid %	Core layer + treated -untreated	Weight loss (Std. dev.) %	Survival rate (Std. dev.) %	Visual rating rank
Virulence controls of pine sapwood			12.50 (0.92)	58.00 (11.54)	4
Control plywood			13.93 (1.73)	38.40 (10.42)	4
−	0.5	+	10.55 (3.05)	38.40 (5.89)	4
−	0.5	−	12.78 (1.75)	37.87 (6.02)	4
10	0.5	+	11.94 (1.12)	29.60 (4.21)	4
10	0.5	−	11.46 (0.83)	31.47 (5.06)	4
−	1	+	10.58 (1.29)	35.2 (6.58)	4
−	1	−	10.40 (2.20)	38.00 (9.32)	4
20	1	+	11.50 (0.53)	25.47 (2.05)	4
20	1	−	10.47 (0.70)	22.00 (4.85)	4

7.2.3.1.3.2 **EN 118**

The results of EN 118 (2014) after EN 84 (1997) are summarized in Table 7.17. The findings of EN 117 and EN 118 were largely close together. All the samples underwent level 4 of attack (Figure 7.23).



From left to right: control, treated with 1% BA, treated with 20% tannin- 1% BA.

Figure 7.23 Some test specimens after EN 118 for beech plywoods made with treated veneers leached by EN 84

The only finding by tannin-boron systems was reduction in the survival rate. The plywood samples made of treated veneers with 20% tannin- 1% BA showed 62.5% reduction in the survival rate compared to the control plywoods when all layers were treated. Interestingly the plywoods with untreated core layer showed approximately same resistance against termite attack, whereas the treated plywoods with tannin-boron systems showed significantly higher weight loss against fungal attack when core layer was left untreated (7.1.3.1.3).

Table 7.17 Results of termite test according to the EN 118 for the beech plywoods made of treated veneers after EN 84. Attack by the subterranean termite *Reticulitermes flavipes* (*ex. santonensis*)

Tannin/Hexamine solution %	Boric acid %	Core layer + treated -untreated	Survival rate (Std. dev.) %	Visual rating rank
Virulence controls of pine sapwood (50 × 25 × 15 mm3)			64.67 (7.82)	4
Control plywood			47.87 (10.33)	4
−	0.5	+	44.40 (6.22)	4
−	0.5	−	42.93 (8.55)	4
10	0.5	+	29.87 (5.14)	4
10	0.5	−	30.67 (8.45)	4
−	1	+	44.80 (3.39)	4
−	1	−	52.67 (3.89)	4
20	1	+	18.40 (7.03)	3,4,4*
20	1	−	20.13 (7.20)	4

* Result of visual rating for the different samples when they are not same

7.2.3.1.3.3 **Choice feeding test**

The results of choice feeding test after EN 84 (1997) are presented in Table 7.18. No difference in the survival rate was observed between treatments. In the containers including alternative samples made of treated veneers with tannin-boron solutions, the control plywood was attacked faster and underwent level 4 of attack.

Interestingly even after EN 84 (1997) there is a clear choice when alternative samples are treated with tannin-boron. The samples treated with this system were eaten by termites with the lower rate.

Table 7.18 Results of choice termite tests for the beech plywood made of treated veneers after EN 84.

	Weight loss (Std. dev.) %	Survival rate (Std. dev.) %	Visual rating rank
1) Control plywood	9.53 (2.69)	39.20 (4.18)	4
2) 0.5% BA	8.08 (3.83)		4, 4, 3*
3) 1% BA	7.42 (1.56)		4
1) Control plywood	10.79 (0.60)	38.80 (7.49)	4
2) 0.5% BA- untreated core	7.47 (2.91)		4, 4, 3
3) 1% BA- untreated core	7.49 (1.96)		4, 4, 3
1) Control plywood	9.36 (0.78)	38.53 (5.03)	4
2) 10% Tannin + 0.5% BA	4.76 (0.56)		3, 3, 4
3) 20% Tannin + 1% BA	5.27 (1.09)		4, 4, 3
1) Control plywood	11.66 (2.84)	40.73 (4.42)	4
2) 10% Tannin + 0.5% BA- untreated core	6.28 (1.97)		3, 3, 4
3) 20% Tannin + 1% BA- untreated core	4.11 (1.08)		3, 3, 4

* Result of visual rating for the different samples when they are not same

7.2.3.2 **Poplar plywood**

7.2.3.2.1 **EN 117**

The results of termites test according to EN 117 are summarized in Table 7.19 for poplar plywoods made from treated veneers before and after leaching tests.

7.2.3.2.1.1 **Before leaching**

Termites attack in control plywoods as well as plywoods made from treated veneers with water caused high weight loss and all samples were subjected to level 4 of degree of attack (Table 7.19). The samples made of treated veneers with BA alone solutions showed very superficial testing nibbles. All termites died in the first week of exposure. The percentage of weight loss was 0% in this treatment. This treatment can be specified as efficient treatment based on the criteria in EN 117 (2013). For the plywoods made of treated veneers with tannin-boron system a deeper area was nibbled by termites.

7.2.3.2.1.2 **After EN 1250-2 (1995)**

After leaching test according to EN 1250-2 the plywood samples made of treated veneers with BA alone solution lost their effectiveness against termites attack and showed high weight loss and survival rate approximately as much as control plywoods (Table 7.19). Also, the plywood samples made of treated veneers with tannin-boron systems present a higher weight loss values than the non-leached ones, but still caused significant mortality. No difference was detected between the results of visual examination between treatments and all samples underwent level 4 of degree of attack. Interestingly, the plywoods made of treated veneers with tannin-boron systems but untreated core layer showed good resistance against termite attack.

7.2.3.2.1.3 **After EN 84 (1997)**

As can be seen, after severe leaching test according to EN 84 the plywood samples made of treated veneers either with tannin-boron system or BA alone solution lost their effectiveness against termites attack and showed high weight loss as much as control plywoods (Table 7.19). The single finding was a few less survivors associated to the plywoods treated with the tannin-boron solution.

Table 7.19 Results of termite test according to the EN 117 for the poplar plywoods made of treated veneers before and after leaching tests. Attack by the subterranean termite *Reticulitermes flavipes* (*ex. santonensis*).

Tannin/Hexamine solution %	Boric acid %	Core layer + treated -untreated	Weight loss (Std. dev.) %	Survival rate (Std. dev.) %	Visual rating rank
Not leached					
Control plywood			26.13 (0.97)	32.93 (3.00)	4
Treated with water			28.25 (4.21)	45.33 (1.51)	4
−	1	+	0	0	1,0,1*
10	1	+	0.64 (0.19)	0	1,1,2
10	1	−	0.58 (0.62)	0	2,1,2
Leached by EN 1250-2					
Control plywood			30.67 (2.63)	47.87 (2.60)	4
−	1	+	29.36 (7.82)	48.13 (7.38)	4
10	1	+	12.01 (5.92)	0.00	4
10	1	−	13.25 (1.55)	3.07 (5.31)	4
Leached by EN 84					
Control plywood			23.14 (0.69)	51.87 (1.29)	4
−	1	+	19.13 (3.17)	50.80 (8.68)	4
10	1	+	19.03 (1.45)	36.67 (4.74)	4
10	1	−	18.62 (4.54)	34.00 (9.83)	4

* Result of visual rating for the different samples when they are not same

7.2.3.2.2 **EN 118**

The results of termites test based on the EN 118 (2014) are presented in Table 7.20 for poplar plywood made with treated veneers before and after leaching tests.

7.2.3.2.2.1 Before leaching

The virulence samples underwent level 4 of attack, but survival rate did not meet standards requirements to confirm validity of the results before leaching. Despite this, the control plywoods showed survival rate as much as when the validity of test was confirmed after EN 84 (Table 7.20).

Control plywoods and plywoods made of treated veneers with water underwent level 4 of attack in the visual examinations and the corresponding survival rate was more than 45%. Similar to EN 117, there was no survivor termite for treated plywoods with BA alone or tannin-boron system. All the termites died after one week from exposure. In the plywoods made of treated veneers with tannin-boron system a deeper area was nibbled by termites and caused higher degree of attack compared to the BA alone solution. The plywood made from treated veneers with 1% BA alone solution meet standard requirements (EN 118, 2014) to be an efficient treatment.

Table 7.20 Results of termite test according to EN 118 for the poplar plywoods made of treated veneers before and after leaching tests. Attack by subterranean termite *Reticulitermes flavipes* (*ex. santonensis*)

Tannin/Hexamine solution %	Boric acid %	Core layer + treated -untreated	Survival rate (Std. dev.) %	Visual rating rank
Not leached				
Virulence controls of pine sapwood (50 × 25 × 15 mm3)			39.20 (6.04)	4
Control plywood			46.53 (7.66)	4
Treated with water			45.33 (1.51)	4
−	0.98	+	0	0,1,1*
8.9	0.98	+	0	2,2,3,
8.9	0.98	−	0	2,2,1
Leached by EN 1250-2				
Virulence controls of pine sapwood			0	4
Control plywood			0	4
−	0.98	+	0	4
8.9	0.98	+	0	4
8.9	0.98	−	0	4
Leached by EN 84				
Virulence controls of pine sapwood			55.60 (5.41)	4
Control plywood			45.31 (12.88)	4
−	0.98	+	49.00 (0.85)	4
8.9	0.98	+	22.80 (9.00)	4
8.9	0.98	−	36.27 (11.80)	4

* Result of visual rating for the different samples when they are not same

7.2.3.2.2.2 **After EN 1250-2**

Similar to the beech plywoods, despite a considerable amount of damage but all termites were abnormally died around two weeks before the end of the test for this set of plywoods. However the virulence controls underwent level 4 of attack but there was no survivor termite at the end. So, the validity of test is not valid.

7.2.3.2.2.3 **After EN 84**

No difference was detected between the results of visual examination and all samples either treated or untreated controls underwent level 4 of degree of attack. Similar to the after EN 1250-2, the plywood samples made of treated veneers with BA alone solution did show any resistant against termite attack. But still the plywood samples made of treated veneers with tannin-boron solution rendered significant mortality of termites particularly when all layers were treated.

7.2.3.2.3 **Choice feeding test**

The results of choice tests for this set of plywoods before and after leaching tests are shown in Table 7.21. The attack of pine sapwood showed that the test is valid (more than 50% survival rate and level 4 of attack). The attack of control plywoods with three samples in each container clearly showed that there was enough pressure on the samples from the termites (high weight loss and level 4 of attack).

Table 7.21 Results of choice termite tests for poplar plywoods made with treated veneers before and after leaching tests

		Weight loss (Std. dev.) %	Survival rate (Std. dev.) %	Visual rating rank
Virulence controls of pine sapwood		13.57 (2.36)	55.47 (4.94)	4
Controls without BA	**1)**Control plywood	11.29 (5.12)	40.60 (1.98)	4, 4, 3*
	2)Control plywood	16.57 (4.79)		4, 4, 4
	3)Control plywood	11.68 (1.09)		4, 4, 4
Before leaching	**1)**Control plywood	16.54 (2.44)	21.33 (25.17)	4, 4, 4
	2)10% Tannin + 1% BA	3.12 (0.90)		2, 2, 1
	3)10% Tannin + 1% BA -untreated core layer	3.93 (1.71)		4, 4, 2
After EN 1250-2	**1)**Control plywood	13.97 (4.98)	36.13 (5.37)	4, 4, 4
	2)10% Tannin + 1% BA	5.10 (1.66)		3, 3, 4
	3)10% Tannin + 1% BA -untreated core layer	10.92 (3.00)		4, 4, 4
After EN 84	**1)**Control plywood	12.88 (7.35)	40.67 (2.83)	4, 4, 3
	2)10% Tannin + 1% BA	7.39 (1.72)		4, 4, 4
	3)10% Tannin + 1% BA -untreated core layer	10.22 (2.06)		4, 4, 4

* Result of visual rating for the different samples when they are not same

The plywood samples made of treated veneers with tannin-boron solutions underwent lower degree of attack before leaching or after mild leaching test (EN 1250-2, 1995), but the control samples were subjected to level 4 of attack. There was no difference in the result of visual examinations after EN 84 and all samples underwent level 4 of attack. High reduction in the survival rate was observed before leaching. Similar to the beech plywoods, the samples treated with tannin-boron systems were eaten with the lower rated and consequently rendered the lower weight loss even after severe leaching test (EN 84, 1997). Despite this fact that borates are not repellent but the result of choice feeding test suggest that treatment with tannin-boron can be partially repellent for termites.

7.2.4 Conclusions for the termite test

The evidence from this study suggests that tannin-boron system can slow down boron leaching. The following conclusions can be drawn from the present study:

1. The results of termites test for poplar plywoods with treated gluelines showed that the amount of BA loading to the glue was not adequate to provide full protection against termite attack. Increase in the BA content of the glue up to 4% caused less survival rate and weight loss but visual rating showed no difference between treatments. All samples underwent level 4 of attack. No notable differences were found between the results of EN 117 (2013) and EN 118 (2014). The results of choice feeding tests for this set of plywoods showed that termites did not make a choice and all samples underwent level 4 of attack.
2. The results of termites test for beech plywoods with treated gluelines showed that the addition of BA and its increase from 5 to 10% reduced the survival rate and the weight loss. No living termite was found associated to the 10% BA in the adhesive. The levels of attack by the visual examination were subject to lower rank following the addition of the BA. The results of EN 118 and EN 117 were largely close together. The results of choice feeding tests showed that despite the lower degree of attack in the some BA containing samples, termites did not make a clear choice between treatments. The containers including samples with BA showed significant reduction in the survival rate, particularly before leaching.

3. The results of termite tests for the beech and poplar plywoods made of treated veneers with tannin-boron system showed satisfactory outcomes. The plywood samples made of treated veneers with BA alone solutions lost their effectiveness against termites attack even after mild leaching test (EN 1250-2). The beech plywoods made of treated veneers with 20% tannin- 1% BA caused significant mortality even after severe leaching test (EN 84).

   The results of choice feeding test for treated veneers plywoods showed that termites made a choice when alternative samples were treated with tannin-boron systems even after vigorous leaching test (EN 84). The control samples were attacked faster and caused greater level of attack. Since borates are not repellent against insects, this result was interesting. There was no choice manner when alternative samples were treated with BA alone solutions. All termites were died at the end of the test, whereas there was control sample in the container. Significant number of survivors at the end of the test was observed when alternative samples were treated with tannin-boron systems even before leaching.

CHAPTER 8: Conclusion and Perspectives

8.1 Looking back

The purpose of the current study was to upgrade resistance of plywood panels made of perishable wood species against fungal or termite attack with low environmental impacts. The newly developed tannin-boron system to reduce the leaching of borates was used for this purpose with two approaches:

(1) Glue line treatment to make plywood for dry condition

It was hypothesized that tannin-hexamine adhesives in alkali environment can be upgrade by adding BA and consequently BA can be partially fixed in this system.

Several adhesives were formulated based on the tannin-hexamine adhesives by the addition of varying amount of BA. Two slow reacting commercial tannins (mimosa and quebracheo tannins) were used in this study. Then these adhesives were used to gluing wood layers to manufacture plywoods for dry uses. The different chemicals, thermomechanical, and physical-mechanical tests were designed to determine the effect of adding BA into the tannin/hexamine adhesive. The biological tests were done before and after leaching tests to evaluate the efficacy of this system on the natural durability and reducing of boron leaching.

(2) Pretreatment of wood veneer to make plywood for humid conditions

In this approach prior to gluing/pressing, wood veneers was treated with different formulations of tannin-boron system. Then theses veneers were bonded together with MUF adhesive to make water resistance and durable plywood for humid conditions (bond class 2). It was expected that this approach can provide effective resistance against biodeterioration agents even after leaching periods.

8.2 Summarizing research findings in relation with the objectives

The findings of this research can be highlighted regarding to different approach of using tannin-boron system.

8.2.1 Results of beech and poplar plywoods with treated glue line

1. The chemicals testing on the adhesives by FTIR and MALDI-TOF analysis enhanced our understanding about the effect of adding BA on the polymerization and chemistry of tannin adhesive. The results of FTIR showed that BA addition can contribute more interflavonoid linkage on the B-rings by the formation of orthodiphenol complexes. The results of MALDI-TOF also perfectly showed the attachment of BA to the flavonoid units. This, in turn, can help to the opening of pyran rings and catalyze the polymerization reactions.
2. The TMA (thermomechanical analysis) experiments confirmed that the addition of BA up to 5% (1) lowered time and temperature of hardening, (2) and also increased MOE values of the adhesive. The reactions were faster with BA when compared with those achieved at same tannin concentration without BA. The addition of 10% BA had the

higher effect on the reduction of hardening time but the peak of maximum MOE drastically decreased.

3. The evaluations of physical and tensile shear strength indicated that up to 5% BA addition into the tannin glue can upgrade physical properties and tensile shear strength. But 10% BA caused imperfect physical and mechanical features. The addition of PMDI resin increased water resistance of tannin glues and caused better physical and mechanical features particularly after soaking in the water. The amount of wood failures visually was higher by BA and PMDI addition compared to the base adhesives (tannin/hexamine) without additives. The tensile shear values obtained for plywoods containing up to 5% BA in the glue met standards requirements for bond class 1 (indoor applications).
4. The addition of borate into the tannin glue increased resistance against fungal attack even after mild leaching test according to the EN 1250-2 (1995). EN 84 (1997) leaching tests caused drastic increase in the weight loss of plywood samples. It looks that all the boron was leached out by this leaching procedure.
5. The minimum toxic thresholds reported in the literatures for BA were lower than values obtained in this study for some set of beech and poplar plywoods with treated gluelines. But, none of these treatments caused weight losses below 3% to be efficient treatments based on the EN 12038 (2003). The data reported in the literatures have been found on the solid wood samples by under pressure treatments. In the pressure treatments (or even simple dipping) the preservative surrounds the samples, whereas in glueline treatment the preservative is added to the glue and bond lines. Hence, the preservatives need to move into the wood for to be effective against biological attack. But when solid wood is treated by a pressure treatment, the growth of fungus is inhibited when fungus attacks to a fully treated wood.
6. The results of termites test for beech and poplar plywoods with treated gluelines showed that the amount of BA loading to the glue up to 5% was not adequate to provide full protection against termite attack. Increase in the BA content of the glue up to 5% caused less survival rate and weight loss but visual rating showed no difference between treatments. All samples underwent level 4 of attack. No notable differences were found between the results of EN 117 (2013) and EN 118 (2014). The results of choice feeding tests for this set of plywoods showed that termites did not make a choice and all samples were strongly attacked. The results of termites test for beech plywoods showed that increase in BA content from 5 to 10% significantly reduced the survival rate and the weight loss. No living termite was found associated to the 10% BA in the adhesive.

Taken together, these results suggest that the addition of BA up to 5% into the tannin/hexamine adhesive can cause significant improvement in the physical properties and bonding quality. On the other hand boron leaching can be partially limited by this approach and provide resistance against decay and degradation even after short-term leaching. A limitation of this study is that the loading of higher amount of BA (10% based on the tannin solids) into the tannin glue causes reduction in the bonding quality and act adversely.

8.2.2 Results of beech and poplar plywoods made of treated veneers

1. The evaluations of physical properties showed that treatments of veneers by tannin-boron system or BA alone solutions did not caused significant difference between treatments. The only significant finding was the lower water absorption of beech plywoods made of treated veneers with 20 tannin+1% BA than in control. This result may be explained by the fact that the formation of the hydrophobic tannin+ hexamine system can greatly reduce water absorption with a strong polymeric network.
2. Tensile shear values of beech and poplar plywood decreased to some extent in the plywoods made of treated veneers with tannin-boron systems. It seems possible that these results are due to the formation of solid hydrophobic tannin-boron network on the surface of treated layers which consequently reduces adhesive contact with the surface of wood layers. On the other hand, the tannin resin causes the surface of the wood smoother and subsequently decreases the roughness for the grip of the adhesive. Despite the negative effect of tannin-boron systems on the tensile shear but all the beech plywoods met standard requirements for bond class 2. Because of poor bonding quality none of the poplar plywood met standard requirements for using in bond class 2 conditions. The MUF adhesive which was used for gluing of poplar veneers was different and had less solid content compared to the experimentally produced MUF used for gluing beech veneers.
3. The plywoods made of treated veneers with tannin-boron solutions showed significant resistance against fungal attack even after EN 1250-2 (1995) and to some extent after EN 84 (1997) depending on the concentration of tannin and BA in the solutions. The best results were obtained with a strong polymeric network of tannin (20% tannin in the formulation). The plywoods with untreated core layer showed lower resistance against fungal attack particularly after leaching tests.
4. The minimum uptake of BA was 0.29% corresponding to the plywoods made from treated veneers with 10% tannin- 0.5% BA when core layer was left untreated. It is higher than values reported in the literatures to be efficient and fully toxic against fungi. The corresponding weight loss for this treatment was 5.26% (before leaching) which is higher than 3% to be efficient treatment. A possible explanation for this can be untreated core layer. On the other hand the values reported in the literature were found on the solid wood. So the action of boron and its diffusion from the surface to the core layer is completely different in plywood. For example, MUF gluelines can play a role like a barrier against water and probably boron diffusion from treated surface layer to untreated core layer.
5. The results of termite tests for the beech and poplar plywoods made of treated veneers with tannin-boron system showed satisfactory outcomes. The plywood samples made with treated veneers with BA alone solutions lost their effectiveness against termites

attack even after mild leaching test (EN 1250-2). The beech plywoods made of treated veneers with 20% tannin- 1% BA caused significant mortality even after severe leaching test (EN 84). The results of choice feeding test for treated veneers plywoods showed that termites made a choice when alternative samples were treated with tannin-boron systems particularly before leaching or after mild leaching conditions.

In general the evidence from this study suggests that tannin-boron systems can slow down the leaching of boron and provide biological resistance after leaching procedure. The limitation of this approach to protect plywood panels is the negative effect of treated veneers on the bonding potential particularly with the higher concentration of tannin.

8.2.3 Perspectives

This research has thrown up many questions in need of further investigation. Based on the positive outcomes of this study and reduction of boron leaching by its addition to the tannin glue, it would be interesting to assess the effects of adding BA to the tannin-formaldehyde adhesive. This adhesive could be applied for exterior applications with the lower formaldehyde emission than the synthetic urea based ones.

Also further studies need to be carried out in order to validate the effect of treatment of veneers with tannin-boron solutions on the other mechanical properties.

Although the current standards for termites test showed high potential to be used for wood-based composites but the design of a new method seems to be necessary. In the service condition, the surfaces of plywoods or other wood-based composites are always exposure to the environments and insect attack similar to the EN 118 conditions. But as subterranean termites prefer eating between sheets so EN 117 are more match with feeding behavior of termites. So a new test method based on the EN 117 but with some modifications seems to be striking. For examples testing samples with sealed edges can be quite interesting by EN 117. On the other hand most of the leaching of preservatives occurs from the edges, whilst the area of the edges in comparison to the surface area in the big panels is negligible and very little. So the evaluations of leaching behavior of tannin-boron systems in the samples with sealed edges might explore more findings. In the general the standard leaching procedures which were used in this study seems to be not compatible with the real service conditions for bond class 1 and 2. In this regards designing a new leaching method looks necessary for bond class 1 and 2. In these service conditions exposed to water or rain are not permanent and is limited. For example, one application for the plywoods in bond class 2 is behind cladding or under roof coverings. Where there is always a possible risk of water dropping on the surface (not submerged in water). Hence, designing of new leaching test in order to simulate this situation looks interesting. A certain amount of water can be drop wise on the samples over certain time for this end.

In the global, the tannin-boron preservatives seems to have high potential for preservation of wood-based composites, in particular plywood, but its efficacy and leaching behavior needs to improve may be by adding some other additives. Also testing with other fast reacting tannin extract like tannins of pine or pecan can probably bring more outcomes.

Bibliography

Abdalla, S., Pizzi, A., Ayed, N., Charrier-El Bouthoury, F., Bertrand, C., Bahabri, F., & Ganash, A. (2014). MALDI-TOF Analysis of Aleppo Pine (Pinus halepensis) Bark Tannin. Bioresource, 9(2), 3396–3406.

Abdel, G., & Skai, E. (2011). Termite damage to buildings : nature of attacks and preventive construction methods. American Journal of Engineering and Applied Sciences, 4(2), 187–200.

Abivardi, C. (2001). Iranian entomology - an introduction, Volume 1: Faunal studies. Volume 2: Applied entomology. Springer-Verlag Berlin Heidelberg. 1033 pp.

Ahmed, B. M., & French, J. R. J. (2005). Report and recommendations of the national termite workshop, Melbourne. Int. Biodeterioration Biodegradation, 56: 69-74.

Ahmed, B. M., French, J. R., & Vinden, P. (2004). Evaluation of borate formulations as wood preservatives to control subterranean termites in Australia. Holzforschung, 58(4), 1–9.

ASTM E84-87 (1998) American Society for Testing and Materials (ASTM). Standard test method for surface burning characteristics of building materials. Philadelphia, PA: ASTM Annual Book of Standards.

Austin, J. W., Szalanski, A. L., Ghayourfar, R., Kence, A., & Gold, R. E. (2006). Phylogeny and genetic variation of Reticulitermes (Isoptera : Rhinotermitidae) from the Eastern Mediterranean and Middle East. Sociobiology, 74(3), 1–19.

Austin, J. W., Szalanski, A. L., Scheffrahn, R. H., Messenger, M. T., Dronnet, S., & Bagnères, A. G. (2005). Genetic evidence for the synonymy of two Reticulitermes Species : Reticulitermes flavipes and Reticulitermes santonensis. Annals of the Entomological Society of America, 98(3), 395–401.

Austin, J. W., Szalanski, A. L., Uva, P., Bagneres, A., & Kence, A. (2002). A comparative genetic analysis of the subterranean termite genus Reticulitermes (Isoptera : Rhinotermitidae). Annals of the Entomological Society of America, 95, 753–760.

Aydin, I. (2014). Effects of veneer drying at high temperature and chemical treatments on equilibrium moisture content of plywood. Maderas. Ciencia Y Tecnología, 16(4), 445–452.

Aydin, I., & Colakoglu, G. (2007). Variation in surface roughness, wettability and some plywood properties after preservative treatment with boron compounds. Building and Environment, 42(11), 3837–3840.

Ayrilmis, N. (2007). Effect of fire retardants on internal bond strength and bond durability of structural fiberboard. Building and Environment, 42(3), 1200–1206.

Badritala, A., Khalil, S., Hashemi, H., Kord, B., Zabihzadeh, S. M., & Safdari, V. (2013). Morphology and mechanical properties of zinc borate-pretreated poplar wood flour/plastic composite. Bioresource, 8(1), 913–922.

Barnes, H. ., & Murphy, R. . (2004). Bending and tensile properties of vapor boron treated composites. Wood and Fiber Science, 37(3), 379–383.

Barnes, H. M. (2012). Durable composites : an overview. In Proc Am Wood Prot Assoc (AWPA), 107, 267–279.

Bertaud, F., Tapin-lingua, S., Pizzi, A., Navarrete, P., & Petit-conil, M. (2012). Development of green adhesives for fibreboard manufacturing using tannins and lignin from pulp mill residues. Cellulose Chemistry and Technology, 46(7-8), 449–455.

Bhatia, T. K. (2002). Use of borate-treated wood as part of an IPM approach for durable and sustainable construction. In S. C. Jones, J. Zhai, & W. H. Robinson (Eds.), Proceedings of the 4th International Conference on Urban Pests, Charleston, SC, USA (Vol. 1993, pp 269–276)

Black, J. M. (1958). The effect of fire-retardant chemicals on glues used in plywood manufacture. Forest Products Laboratory - USDA Forest Service, Report No. 1427, 7 pp.

Braghiroli, F. L., Fierro, V., Izquierdo, M. T., Parmentier, J., Pizzi, A., & Celzard, A. (2014). Kinetics of the hydrothermal treatment of tannin for producing carbonaceous microspheres. Bioresource Technology, 151, 271–277.

Bridaux, V., Charrier, B., Fauroux, N., Charrier, F., & Goncalez, J. (2001). Addition of boron based compound in the LVL glueline: effect on the mechanical properties and the leaching of boron. Holzforschung, 55(5), 559–562.

Brunet, J., Fritz, Ö., & Richnau, G. (2010). Biodiversity in European beech forests – a review with recommendations for sustainable forest management. Ecological Bulletins, 53, 77–94.

Caldeira, F. (2010). Boron in wood preservation–a review in its physico-chemical aspects. Silva Lusitana, 18(2), 179–196.

Cameron, S. L., & Whiting, M. F. (2007). Mitochondrial genomic comparisons of the subterranean termites from the Genus Reticulitermes (Insecta: Isoptera: Rhinotermitidae). Genome, 50(2), 188–202.

Clausen, C. A. (2010). Biodeterioration of wood. In Wood Handbook: Wood as an engineering material (pp. 14.1–14.16). Madison, Wisconsin, Centennial Edition, General Technical Report FPL.

Clausen, C. A. (2012). Enhancing durability of wood-based composites with nanotechnology. General Technical Report, FPL-GTR-218. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 8–12 p.

Clément, J. L., Bagnères, A. G., Uva, P., Wilfert, L., Quintana, a., Reinhard, J., & Dronnet, S. (2001). Biosystematics of Reticulitermes termites in Europe: morphological, chemical and molecular data. Insectes Sociaux, 48(3), 202–215.

Colakoglu, G., Colak, S., Aydin, I., Yildiz, U. C., & Yildiz, S. (2003). Effect of boric acid treatment on mechanical properties of laminated beech veneer lumber. Silva Fennica, 37(4), 505–510.

Çolakoğlu, G., & Demirkir, C. (2006). Characteristics of plywood panels produced with urea formaldehyde resin containing borax. Holz Als Roh- Und Werkstoff, 64(3), 250–251.

Di, L., Wang, C., Wu, J., Wan, L.-S., & Xu, Z.-K. (2011). Progress in boric acid based saccharide sensors. Chinese Journal of Analytical Chemistry, 39(4), 592–598.

Drysdale, J. A. (1994). Boron treatments for the preservation of wood: A review of efficacy data for fungi and termites. In International Research Group on wood preservation. IRGWP-94-30037, Bali, Indonesia.

Eaton, R. A., & Hale, M. D. (1993). Wood: decay, pests and protection.Chapman and Hall Ltd. 546 pp.

Elisashvili, V., Irbe, I., & Andersone, I. (2012). Hydrolytic enzyme activity of EN113 standard basidiomycetes in the fermentation of lignocellulosic material and wood colonization. Holzforschung, 66(7), 841–847.

Efhamisis, D., Hamzeh, Y., Thevenon, M. F., Pizzia, A., Karimi, A. N., & Pourtahmasi, K. (2015). Accelerated Autocondensation of Quebracho Tannin Wood Adhesive by Boric Acid. Iraninan Journal of Forest and Wood Product, 68(1), 149–160.

EN 113. (1996). Wood preservatives—Test method for determining the protective effectiveness against wood destroying basidiomycetes—Determination of the toxic values.

EN 117. (2005). Wood preservatives – Determination of toxic values against Reticulitermes species (European termites) (Laboratory method).

EN 118. (2005). Wood preservatives – Determination of preventive action against Reticulitermes species (European termites) (Laboratory method).

EN 314-1. (2004). Plywood -Bonding quality -Part 1: Test methods.

EN 314-2. (1993). Plywood -Bonding quality- Part 2: Requirements.

EN 317. (1993). Particleboards and fibreboards- Determination of swelling in thickness after immersion in water.

EN 322. (1993). Wood-based panels - Determination of moisture content.

EN 323. (1993). Wood-based panels. Determination of density.

EN 335. (2013) Durability of wood and wood-based products. Use classes: definitions, application to solid wood and wood-based products.

EN 335-3. (1996). Durability of wood and wood-based products - Definition of hazard classes of biological attack.

EN 350-1 (1994) Durability of wood and wood-based products – Natural durability of solid wood: guide to the principles of testing and classification of the natural durability of wood.

EN 47. (2005). Wood preservatives. Determination of the toxic values against larvae of Hylotrupes bajulus (Linnaeus) (Laboratory method).

EN 636. (2003). Plywood - Specifications.

EN 84. (1997). Wood preservatives-accelerated ageing of treated wood prior to biological testing. Leaching procedure.

EN1250-2. (1995). Wood preservatives. Methods of measuring losses of active ingredients and other preservative ingredients from treated timber. Laboratory method for obtaining samples for analysis to measure losses by leaching into water or synthetic sea water.

ENV 12038. (2003). Durability of wood and wood-based products - wood-based panels - method of test For determining the resistance against wood-destroying basidiomycetes.

FAO. (2000). Termite Biology and Management Workshop. United Nations Food and Agriculture Organization, Report of the UNEP/FAO/Global IPM Facility, February 1-3, Geneva, Switzerland.

FAO. (2013). Global Forest Products Facts and Figures. FAOSTAT (available at Faostat.fao.org).

Foo, L. Y., & Karchesy, J. J. (1989). Chemical nature of phlobaphenes. In R. W. Hemingway, J. J. Karchesy, & S. J. Branham (Eds.), Chemistry and significance of condensed tannins (pp. 109–118). Springer US.

Freeman, M. H., Mcintyre, C. R., & Jackson, D. (2009). A critical and comprehensive review of boron in wood preservation. In proceedings of the American Wood Protection Assoc. (Vol. 105, 279–294).

Gardner, D. J., Tascioglu, C., & Walinder, M. E. (2003). Wood composite protection. In T. P. S. B. Goodell, D.D. Nicholas (Ed.), Wood composite protection (pp. 399–419). Washington D.C., American chemical society.

Ghasemi, R., & Modirrahmati, A. (2004). Valuation of different poplar timber production in Karaj. Iranian Journal of Forest and Poplar Research, 12(2), 221–249.

Hill, C. A. S. (2006). Wood modification (1st ed.). John Wiley & Sons. 260 pp.

Humar, M., & Lesar, B. (2008). Fungicidal properties of individual components of copperethanolamine-based wood preservatives. International Biodeterioration & Biodegradation, 62(1), 46–50.

Humar, M., Pohleven, F., & Amartey, S. a. (2004). Influence of boron in CCB formulation on growth and decay capabilities of copper tolerant fungi. Holz Als Roh- Und Werkstoff, 62(3), 177–180.

ISO 3696. (1987). Water for analytical laboratory use - Specification and test methods.

JIS K 1571. (2004). (English): Wood preservatives -Performance requirements and their test methods for determining effectiveness.

Jordan, B. (2012). Leachability of borate treated southern pine influenced by copper naphthenate treatment. Marshall Plan Scholarship Papers, Salzburg Uiversity, 1–20. DOI: http://www.marshallplan.at/images/papers_scholarship/2012/Jordan_2012.pdf.

Jorma, J. (2010). The international promotion of wood construction as a part of climate policy. Working Group Report. Finland, 46 pp.

Kamoun, C., & Pizzi, A. (2000). Mechanism of hexamine as a non-aldehyde polycondensation resins hardener. Part 1: Hexamine decomposition and reactive intermediates. Holzforschung Und Holzverwertung, 52(1), 16–19.

Kamoun, C., Pizzi, A., & Zanetti, M. (2003). Upgrading melamine–urea–formaldehyde polycondensation resins with buffering additives. I: The effect of hexamine sulfate and its limits. Journal of Applied Polymer Science, 90(1), 203–214.

Kartal, N. S., Ayrilmis, N., & Imamura, Y. (2007). Decay and termite resistance of plywood treated with various fire retardants. Building and Environment, 42(3), 1207–1211.

Kartal, S. N., Hwang, W.-J., Shinoda, K., & Imamura, Y. (2004). Decay and termite resistance of wood treated with boron-containing quarternary ammonia compound, didecyl dimetyl ammonium tetrafluoroborate (DBF) incorporated with acryl-silicon type resin. In The International Research Group on Wood Preservation, IRG/WP 04-03334. Ljubljana, Slovenia.

Kartal, S. N., & Imamura, Y. (2004). Effects of N-N-(1, 8-Naphthalyl) hydroxylamine (NHA-Na) and hydroxynaphthalimide (NHA-H) on boron lechability and biological degradation of wood. Holz Als Roh- Und Werkstoff, 62(5), 378–386.

Khouadja, A., & Barens, H. M. (2001). Treatment and redrying of western hemlock plywood. Forest Products Journal, 51(1), 74–80.

Kim, S. (2009). Environment-friendly adhesives for surface bonding of wood-based flooring using natural tannin to reduce formaldehyde and TVOC emission. Bioresource Technology, 100(2), 744–8.

Kim, S., & Kim, H. J. (2003). Curing behavior and viscoelastic properties of pine and wattle tannin-based adhesives studied by dynamic mechanical thermal analysis and FTIR-ATR spectroscopy. Journal of Adhesion Science and Technology, 17(10), 1369–1383.

Kirkpatrick, J. W., & Barnes, H. M. (2006). Biocide Treatments for Wood Composites - A Review. In The International Research Group on Wood Protection, IRG/WP, 6, 40323. Tromsoe, Norway.

Korb, J., & Hartfelder, K. (2008). Life history and development-a framework for understanding developmental plasticity in lower termites. Biological Reviews of the Cambridge Philosophical Society, 83(3), 295–313.

Kralj, P., Humar, M., & Lesar, B. (2010). Influence of polyethylene and oxidized polyethylene wax emulsions on leaching dynamics of boric acid from impregnated spruce wood. Drvna Industrija, 61(4), 213–221.

Laks, P. E. (1999). The past, present, and future of preservative-containing composites. In D. F. B. M. P. Wolcott, R. Tichy (Ed.), 33rd International Particleboard/Composite Materials Symposium Proceedings (pp. 151–158). Pullman, WA., Washington State University.

Laks, P. E. (2002). Biodegradation susceptibility of untreated engineered wood products. In Enhancing the Durability of Lumber and Engineered Wood Products. FPS Symposium Proceedings No. 7249. (pp. 125–130). Madison, WI: Forest Products Society.

Lebow, S. (2004). Alternatives to chromated copper arsenate for residential construction. Res. Pap. FPL-RP-618. Madison, WI: U.S. Department of Agriculture, Forest Service-Forest Products Laboratory.

Lebow, S., Kirker, G., White, R., Amburgey, T., Barnes, H. M., Sanders, M., & Morrell, J. (2012). Guide for in-place treatment of wood in historic covered and modern bridges. General Technical Report FPL-GTR-205. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.

Lebow, S. T. (2010). Wood Handbook, Chapter 15: Wood preservation. General Technical Report FPL-GTR-190. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, 43p.

Lee, S., Wu, Q., & Smith, W. R. (2004). Formosan subterranean termite resistance of borate-modified strandboard manufactured from southern wood species: a laboratory trial. Wood and Fiber Science, 36(1), 107–118.

Lee, S. Y., & Wu, Q. (2007). Leachability of zinc borate-modified oriented strandboard. Mokchae Knoghak, 35(5), 46–57.

Lesar, B., Pohleven, F., & Humar, M. (2010). Use of boron compounds for treatment of wooden historical objects. In Proceedings: Wood Science for Conservation of Cultural Heritage (pp. 2–6). Hamburg/Germany.

Lesar, B., Ugovsek, A., Kariz, M., & Sernek, M. (2011). Influence of boron compounds in adhesives on the bonding quality and fungicidal properties of wood. Wood Research, 56(3), 385–392.

LeVan, S. L., & Winandy, J. E. (1990). Effects of fire retardant treatments on wood strength: a review. Wood and Fiber Science, 22(1), 113–131.

Lewis, V. R. (2008). Isoptera. In H. R. Vincent and T. C. Ring (Eds), Encyclopedia of Insects, 2nd Edn. (pp. 531– 534). New York: Academic Press.

Lloyd, J. d. (1997). International status of borate perservative systems. In the seconed international conference on wood protection with diffusible preservatives and pesticidesed. Forests Products Society (pp. 45–54). Alabama.

Lloyd, J. D., Dickinson, D. J., & Murphy, R. J. (1990). The probable pechanisms of action of boric acid and borates as wood preservatives. In International Research Group on Wood Preservation. IRG/WP/1450. Stockholm, Sweden.

Lloyd, J. D., Fogel, J. L., & Vizel, A. (2001). The use of zirconium as an inert fixative for borates in preservation. In The International Research Group on Wood Preservation. IRG/WP 01-30256. Nara, Japan.

Lloyd, J. D., Schoeman, M. W., & Stanley, R. (1998). Remedial timber treatment with borates. In W. H. Robinson, F. Rettich, & G. W. Rambo (Eds.), 3rd international conference on urban pests (pp. 415–423). Czech Republic.

Luo, J., Chen, H., & Morrell, J. J. (2005). Effect of borate on uptake and efficacy of an anti-sapstain treatment. In The International Research Group on Wood Protection. IRG/WP 05-30380. Bangalore, India.

Lyon, F., Thevenon, M. F., Hwang, W. J., Imamura, Y., Gril, J., & Pizzi, A. (2007). Effect of an oil heat treatment on the leachability and biological resistance of boric acid impregnated wood. Annals of Forest Science, 64(6), 673–678.

Manning, M. J. (2002). Wood protection processes for engineered wood products. In Enhancing the Durability of Lumber and Engineered Wood Products. FPS Symposium Proceedings. Forest Products Society. (pp. 131–136.). Madison, WI.

McClary, C. A., & Taylor, M. S. (2013). Applications of organoboron compounds in carbohydrate chemistry and glycobiology: analysis, separation, protection, and activation. Carbohydrate Research, 381, 112–22.

McCutcheon, S., Smith, M. G., Palfreyman, J. W., & Durrant, P. (1996). Effects of boron treatments on partially decayed oak and pitch pine heartwood. In International Research Group on Wood Preservation. IRG/WP 96-30106. Guadeloupe, France.

Meikleham, N., Pizzi, A., & Stephanou, A. (1994). Induced accelerated autocondensation of polyflavonoid tannins for phenolic polycondensates. I. 13C-NMR, 29Si-NMR, X-ray, and polarimetry studies and mechanism. Journal of Applied Polymer Science, 45(12), 1827–1845.

Micklewright, J. T. (1998). Wood preservation statistics - 1997. Prepared for the American Wood Preservers Association (AWPA), Granbury, TX.

Modaberi, A., Adeli, K., & Soosani, J. (2014). Evaluating Populus nigra absolute age of exploitation with different planting distances in the central zagros. Philippine Scientist Journal, 52(1), 56–61.

Moubarik, A., Mansouri, H. R., Pizzi, A., Charrier, F., Allal, A., & Charrier, B. (2013). Corn flour-mimosa tannin-based adhesives without formaldehyde for interior particleboard production. Wood Science and Technology, 47(4), 675–683.

Moubarik, A., Pizzi, A., Allal, A., Charrier, F., & Charrier, B. (2009). Cornstarch and tannin in phenol-formaldehyde resins for plywood production. Industrial Crops and Products, 30(2), 188–193.

Murphy, R. J., Dickinson, D. J., Turner, P., Wickens, P. J., & Hashin, R. (1993). Vapor boron treatment of wood composites: production of wood- based composite products. In IUFRO Symposium on Protection of Wood-Based Composite Products, Orlando, FL, Forest Products Society (pp. 49–56), Madison, WI.

Nair, S. S. (2006). Effectiveness of copper-boron diffusion treatment for wood. In Partial Fulfillment of the Requirements for the Degree of Master of Science with a Major in Forest Products in the College of Graduate Studies University of Idaho.

Obanda, D. N., Shupe, T. F., & Barnes, M. H. . (2008). Reducing leaching of boron-based wood preservatives - a review of research. Bioresource Technology, 99(15), 7312–22.

Osman, Z. (2012). Thermomechanical analysis of the tannins of Acacia Nilotica spp. Nilotica as a rapid tool for the evaluation of wood–based adhesives. Journal of Thermal Analysis and Calorimetry, 107(2), 709–716.

Özdemir, F., & Tutuş, A. (2013). Effects of fire retardants on the combustion behavior of high-density fiberboard. Bioresource, 8(2), 1665–1674.

Palanti, S., & Feci, E. (2013). A wood preservative based on commercial silica nanodispersions and boric acid against fungal decay through laboratory and field tests. Open Journal of Forestry, 03(02), 57–61.

Pantoja-Castro, M. A., & González-Rodríguez, H. (2011). Study by infrared spectroscopy and thermogravimetric analysis of tannins and tannic acid. Revista Latinoamericana de Química, 39(3), 107–112.

Pasch, H., Pizzi, A., & Rode, K. (2001). MALDI±TOF mass spectrometry of polyfavonoid tannins. Polymers, 42(01), 7531–7539.

Pichelin, F., Nakatani, M., Pizzi, A., Wieland, S., Despres, A., & Rigolet, S. (2006). Structural beams from thick wood panels bonded industrially with formaldehyde-free tannin adhesives. Forest Products Journal, 56(5), 31–36.

Ping, L., Pizzi, A., Guo, Z. D., & Brosse, N. (2012). Condensed tannins from grape pomace: Characterization by FTIR and MALDI TOF and production of environment friendly wood adhesive. Industrial Crops and Products, 40 (1), 13–20.

Pizzi, A. (2006). Recent developments in eco-efficient bio-based adhesives for wood bonding: opportunities and issues. Journal of Adhesion Science and Technology, 20(8), 829–846.

Pizzi, A. (1994). Hardening mechanism of tannin adhesives with hexamine. Holz Als Roh- Und Werkstoff, 52(4), 229–229.

Pizzi, A. (1994). Tannin-based wood adhesives. In A. Pizzi (Ed.), Wood adhesives chemistry and technology (pp. 149–217). New York: Marcel Dekker Inc.

Pizzi, A. (2003). Natural phenolic adhesives I. In A. Pizzi & K. L. Mittal (Eds.), Handbook of adhesive technology (2nd edn., pp. 573–587). New York: Marcel Dekker.

Pizzi, A., & Baecker, A. (1996). A new boron fixation mechanism for environment friendly wood preservatives. Holzforschung, 50(6), 507–510.

Pizzi, A., Meikleham, N., Dombo, B., & Roll, W. (1995a). Autocondensation-based, zero-emission, tannin adhesives for particleboard. Holz Als Roh- Und Werkstoff, 53(3), 201–204.

Pizzi, A., Meikleham, N., & Stephanou, A. (1995b). Induced accelerated autocondensation of polyflavonoid tannins for phenolic polycondensates. II. Cellulose effect and application. Journal of Applied Polymer Science, 55(6), 929–933.

Pizzi, A., Stracke, P., & Trosa, A. (1997). Industrial tannin/hexamine low-emission exterior particleboards. Holz Als Roh- Und Werkstoff, 55(2), 168–168.

Pizzi, P. A. (1983). Tannin-based wood adhesives. In A. Pizzy (Ed.), Wood adhesives chemistry and technology (pp. 177–246.). New York: Marcel Dekker Inc.

Puică, N. M., Pui, A., & Florescu, M. (2006). FTIR spectroscopy for the analysis of vegetable tanned ancient leather. European Journal of Science and Theology, 2(4), 49–53.

Rahimzadeh, A., Rashid, M., Garjan, A. S., & Naseri, B. (2012). Laboratory evaluation of Metarhizium anisopliae (Metschnikoff) for controlling Amitermes vilis (Hagen) and Microcerotermes gabrielis (Weidner) (Isoptera : Termitidae). Journal of Crop Protection, 1(1), 27–34.

Ravan, S. (2010). Ecological distribution and feeding preferences of Iran termites. African Journal of Plant Science, 4(9), 360–367.

Rayner, A. D. M., & Boddy, L. (1988). Fungal decomposition of wood: Its biology and ecology (1 edition). Wiley , 602 pp.

Reid, H., Huq, S., Inkinen, A., Macgregor, J., Mayers, J., Murray, L., & Tipper, R. (2004). using wood products to mitigate climate change: a review of evidence and key issues for sustainable, International Institute for Environment and Development, 90 pp.

Reinprecht, L. (2010). Fungicides for wood protection – World viewpoint and evaluation / testing in Slovakia. In O. Carisse (Ed.), Fungicides (pp. 95–122). InTech.

Richardson, B. A. (2002). Wood preservation. Routledge. 226 pp.

Ross, A. S., Ward, H. A., & Smith, W. R. (2003). An overview on new generation of preservation treatments for wood-based panels and other engineered wood products. In the 7th European Panel Products Symposium (pp. 219–225), Llandudno, UK.

Salman, S., Pétrissans, A., Thévenon, M. F., Dumarçay, S., Perrin, D., Pollier, B., & Gérardin, P. (2014). Development of new wood treatments combining boron impregnation and thermo modification: effect of additives on boron leachability. European Journal of Wood and Wood Products, 72(3), 355–365.

Sathre, R., & Gustavsson, L. (2009). A state-of-the-art review of energy and climate effects of wood product substitution, School of Technology and Design, Report No. 57, Växjö University, Sweden, 59 pp.

Schmidt, O. (2006). Wood and tree fungi- Biology, damage, protection, and use. Springer-Verlag Berlin Heidelberg, 334 pp.

Schoeman, M. W., & Lloyd, J. D. (1998). International standardisation: a hypothetical case study with stand-alone borate wood preservatives. In International Research Group on Wood Preservation, IRG/WP 98-20147. Stockholm, Sweden.

Schwarze, F. W. M. R. (2007). Wood decay under the microscope. Fungal Biology Reviews, 21(4), 133–170.

Sealy-Fisher, V. J., & Pizzi, A. (1992). Increased pine tannins extraction and wood adhesives development by phlobaphenes minimization. Holz Als Roh- Und Werkstoff, 50(5), 212–220.

Sedaghati Zade, K., PashaeeRad, S., Ghayour Far, R., & Sheydaee, M. (2013). Statistical Analyses of Termite Population of Anacanthotermes vagans in Golestan Province (Isoptera:Hodotermitidae). Journal of Experimental Animal Biology (IN PERSIAN), 5(1), 43–50.

Sensogut, C., Ozalp, M., & Yesil, H. (2009). The effect of borax pentahydrate addition to urea formaldehyde on the mechanical characteristics and free formaldehyde content of plywood. International Journal of Adhesion and Adhesives, 29(5), 589–592.

Shi, S., & Walker, J. (2006). Wood-based composites plywood and veneer-based products, In J. C. F Walker (Ed.) Primary wood processing, (pp. 391–426). Amsterdam: Springer-Verlag Berlin Heidelberg.

Shmulsky, R., & Jones, P. D. (2011). Forest Products and Wood Science (6th ed.). Wiley-Blackwell. 496 pp.

Siemiatycki, J., Richardson, L., Straif, K., Latreille, B., Lakhani, R., Campbell, S., Rousseau M.C., & Boffetta, P. (2004). Listing occupational carcinogens. Environmental health perspectives, 1447-1459.

Simonsen, J., Freitag, C. M., Silva, a., & Morrell, J. J. (2004). Wood/plastic ratio: Effect on performance of borate biocides against a brown rot fungus. Holzforschung, 58(2), 205–208.

Smith, W. R., & Wu, Q. (2005). Durability improvement for structural wood composites through chemical treatments current state of the art. Forest Products Journal, 55(2), 8–17.

Stalker, I. N., & Milton, F. T. (1994). The Preservation of Wood: A Self Study Manual For Wood Treaters. University of Minnesota Extension Service, Unstated edition, 102 pp.

Tascioglu, C., & Tsunoda, K. (2010). Biological performance of copper azole-treated wood and wood-based composites. Holzforschung, 64(3), 399–406.

Tascioglu, C., & Tsunoda, K. (2012). Retention of copper azole and alkaline copper quat in wood-based composites post-treated by vacuum impregnation. Wood Research, 57(1), 101–110.

Tascioglu, C., Yoshimura, T., & Tsunoda, K. (2013). Biological decay and termite resistance of post-treated wood-based composites under Protected above-ground conditions : a preliminary study after 36 months of exposure. Bioresource, 8(1), 833–843.

Terzi, E., Kartal, S. N., Erilkun, B., & Imamura, Y. (2011). Preliminary evaluation of boron release and biological resistance of wood treated with disodium octoborate tetrahydrate (DOT) and a water-repellent compound. African Journal of Biotechnology, 10(10), 1833–1839.

Thébault, M., Pizzi, A., Essawy, H. A., Barhoum, A., & Assche, G. Van. (2015). Isocyanate free condensed tannin-based polyurethanes, 67(1), 513–526.

Theis, M., & Grohe, B. (2002). Biodegradable lightweight construction boards based on tannin/hexamine bonded hemp shaves. Holz Als Roh- Und Werkstoff, 60(4), 291–296.

Thevenon, M. F., Tondi, G., & Pizzi, A. (2009). High performance tannin resin-boron wood preservatives for outdoor end-uses. European Journal of Wood and Wood Products, 67(1), 89–93.

Thevenon, M. F., Tondi, G., & Pizzi, A. (2010). Friendly wood preservative system based on polymerized tannin resin-boric acid for outdoor applications. Maderas. Ciencia Y Tecnología, 12(3), 253–257.

Tondi, G., Wieland, S., Lemenager, N., Petutschnigg, A., Pizzi, A., & Thevenon, M. F. (2012a). Efficacy of tannin in fixing boron in wood fungal and termite resistance. BioResources, 7(1), 1238–1252.

Tondi, G., Wieland, S., Wimmer, T., Thevenon, M. F., Pizzi, A., & Petutschnigg, A. (2012b). Tannin-boron preservatives for wood buildings: mechanical and fire properties. European Journal of Wood and Wood Products, 70(5), 689–696.

Tondi, G., Palanti, S., Wieland, S., Thevenon, M. F., Petutschnigg, A., & Schnabel, T. (2012c). Durability of tannin-boron-treated timber. BioResources, 7(4), 5138–5151.

Tondi, G., Thevenon, M. F., Mies, B., Standfest, G., Petutschnigg, a., & Wieland, S. (2013). Impregnation of Scots pine and beech with tannin solutions: effect of viscosity and wood anatomy in wood infiltration. Wood Science and Technology, 47(3), 615–626.

Tsunoda, K. (2001). Preservative properties of vapor-boron-treated wood and wood-based composites. Journal of Wood Science, 47(2), 149–153.

Turner, P., Murphy, R. J., & Dickinson, D. J. (1990). Treatment of wood based panel products with volatile borates. In International Research Group on Wood Preservation document no. IRG/WP/3616. Rotorua, New Zealand.

Van Langenberg, K., Grigsby, W., & Ryan, G. (2010). Green Adhesives : Options for the Australian industry – summary of recent research into green adhesives from renewable materials and identification of those that are closest to commercial uptake. In Forest & Wood Products Australia, Project Number: PNB158-0910, FWPA (Vol. 61, pp. 10–16).

Verma, M., Sharma, S., & Rajendra, P. (2009). Biological alternatives for termite control: A review. International Biodeterioration & Biodegradation, 63(8), 959–972.

Wagner, M. R., Cobbinah, J. R., & Paul P. Bosu. (2008). Forest entomology in West tropical Africa: Forests Insects of Ghana (2nd Edn). New York, Springer. 244 pp.

Weidner, V. H. (1959). Die Termiten von Afghanistan, Iran und Irak (Isoptera) . Abhandl v. Verhandl Naturwissenschaftl. Verens, Hamburg. Mit 22 Abbildungen, Davon Abb. 2 Und 7 Auf Tafel II, 43–70.

Williams, L. H., & Amburgey, T. L. (1987). Integrated protection against lyctid beetle infestations: IV. Resistance of boron-treated wood to insect and fungal attack. Forest Products Journal, 37(2), 10–17.

Winandy, J. E., LeVan, S. L., Schaffer, E. L., & Lee, P. W. (1988). Effect of fire-retardant treatment and redrying on the mechanical properties of douglas-fir and aspen plywood. Research Paper, FPL-RP-485, Forest Service, Forest Products Laboratory, U.S. Department of Agriculture, Madison, WI, 20 P.

Wood The fuel of the future. (2013). DOI: http://www.economist.com/news/business/21575771-environmental-lunacy-europe-fuel-future

Wu, Q. (2004). Preservative-treated structural wood composites for durable home construction. Position Paper in Proc. NSF and HUD Housing Research Workshop, Orlando, FL. February 11-14, 200–208.

Wu, Q., Lee, S., & Lee, J. N. (2002). Mechanical, physical, and biological properties of borate-modified oriented strandboard. In Proc. International Conference on Advances in Building Technology. Hong Kong, China.

XP CEN/TS 15083-1. (2006). Durability of wood and wood based products. Determination of solid wood durability against wood destroying fungi Test methods. Part 1: Basidiomycetes.

Xu, X., Lee, S., Wu, Y., & Wu, Q. (2013). Borate-treated strandboard from southern wood secies: resistance against decay and mold fungi. Bioresource, 8(1), 104–114.

Youngquist, J. A. (2010). Wood-based composites and panel products. In wood handbook wood as an engineering material (pp. 11.1-11.28). Madison, Wisconsin, Centennial Edition, General Technical Report FPL.

Zabel, R. A., & Morrell, J. J. (1992). Wood microbiology: decay and its prevention. Academic Press. 476 pp.

Zhou, X., Pizzia, A., & Dub, & G. (2012). The Effect of nanoclay on melamine-urea-formaldehyde wood adhesives. Journal of Adhesion Science and Technology, 26(10-11), 34–40.

Zobel, B. (1984). The changing quality of the world wood supply. Wood Science and Technology, 18(1), 1–17.

Annex A. Cutting Pattern and sampling of the plywood panels

Figure A.1 Schematic diagram of the cutting pattern of boards

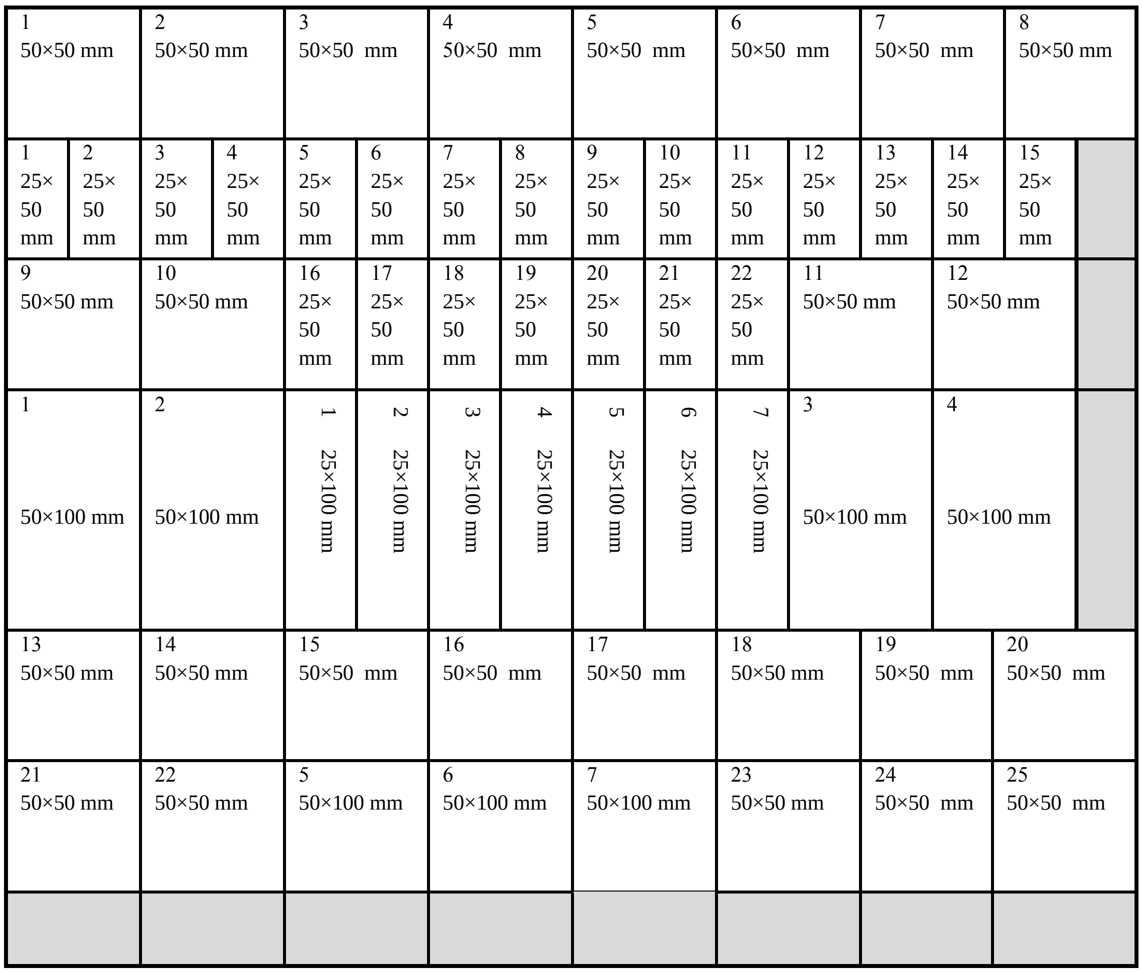


Table A.1 Plywood properties studied and the corresponding standards and test samples size

Property	Sample size mm (length × width)	Standard
Density	50 × 50	EN 323
MC%	50 × 50 & 50 × 25	EN 322
Thickness swelling, water absorption and dimension change	50 × 50	EN 317
Tensile shear strength	100 × 25	EN 314-1
Field test	100 × 50	-
Termite test	50 × 50	EN 118
Termite test	50 × 25	EN 117
Fungal test	50 × 50	ENV 12038

Annex B. Guidelines for visual examination

B.1 Guidelines for visual examination according to EN 117 (2013) and EN 118 (2014)

The guidelines for both standards are same but in EN 118 (2014) only limited surface of samples is exposed to the termite attack. The surface area for EN 118 is around 450 mm^2. In EN 117 (2013) all surfaces of sample should considered as surface area.

The test samples after termite test were visually rated by any evidence of attack, its extent and its depth, in according with the following schedule:

0) No attack

1) Attempted attack
   i. Superficial erosion of insufficient depth to be measured on an unlimited area of the test specimen; or
   ii. Attack to a depth of 0.5 mm provided that this is restricted to an area or areas not more than 30 mm^2 in total; or
   iii. Combination of i and ii
2) Slight attack
   i. Erosion of 1 mm in depth limited to not more than 1/10 of the surface area of the test specimen; or
   ii. Single tunneling to a depth of up to 3 mm; or
   iii. Combination of i and ii
3) Average attack
   i. Erosion of < 1 mm in depth over more than 1/10 of the surface area of the test specimens; or
   ii. Erosion of > 1 mm to < 3 mm in depth limited to not more than 1/10 of the surface area of the test specimens; or
   iii. Isolated tunneling of a depth > 3 mm not enlarging to form cavities; or
   iv. Any combination of i, ii or iii
4) Strong attack
   i. Erosion of > 1 mm to < 3 mm in depth of more than 1/10 of the surface area of the test specimens; or
   ii. Tunneling penetrating to a depth > 3 mm and enlarging to form a cavity in the body of the test specimen; or
   iii. Combination of i and ii

Annex C. Statistical analysis

C.1: Statistical analysis for physical properties and tensile shear

Table C.1 Result of two-way ANOVA test for oven dry density and condoning density of poplar plywoods with treated glueline

Conditioning Density					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	0.01	14	0.00	0.57	0.89
Intercept	38.60	1	38.60	39832.19	0.00
Tannin concentration (1)	0.00	2	0.00	0.77	0.46
Formulations (2)	0.00	4	0.00	0.68	0.61
(1) × (2)	0.00	8	0.00	0.46	0.88
Error	0.16	165	0.00		
Total	38.76	180			
Corrected Total	0.17	179			
R Squared = .046 (Adjusted R Squared = -.035)					
Oven dry Density					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	0.00	14	0.00	0.25	1.00
Intercept	16.56	1	16.56	20249.85	0.00
Tannin concentration (1)	0.00	2	0.00	0.32	0.73
Formulations (2)	0.00	4	0.00	0.42	0.79
(1) × (2)	0.00	8	0.00	0.15	1.00
Error	0.06	135	0.00		
Total	16.62	150			
Corrected Total	0.06	149			
R Squared = .044 (Adjusted R Squared = -.134)					

Table C.2 Result of two-way ANOVA test for water absorption after 2 and 24 hours for poplar plywoods with treated glueline

Water absorption after 2 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	456.22	14	32.59	0.54	0.90
Intercept	146288.1	1	146288.12	2417.35	0.00
Tannin concentration (1)	111.01	2	55.51	0.92	0.40
Formulations (2)	142.37	4	35.59	0.59	0.67
(1) × (2)	202.83	8	25.35	0.42	0.91
Error	4538.69	135	60.52		
Total	151283	150			
Corrected Total	4994.922	149			
a	R Squared = .091 (Adjusted R Squared = -.078)				
Water absorption after 24 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	1668.78	14	119.20	1.04	0.42
Intercept	608507.2	1	608507.16	5311.56	0.00
Tannin concentration (1)	814.35	2	407.18	3.55	0.03
Formulations (2)	251.88	4	62.97	0.55	0.70
(1) × (2)	602.54	8	75.32	0.66	0.73
Error	8592.20	135	114.56		
Total	618768.2	150			
Corrected Total	10260.99	149			
a	R Squared = .163 (Adjusted R Squared = .006)				

Table C.3 Result of two-way ANOVA test for thickness swelling after 2 and 24 hours for poplar plywoods with treated glueline

Thickness swelling after 2 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	67.05	14	4.79	1.92	0.04
Intercept	3744.79	1	3744.79	1501.71	0.00
Tannin concentration (1)	34.41	2	17.21	6.90	0.00
Formulations (2)	27.36	4	6.84	2.74	0.03
(1) × (2)	5.28	8	0.66	0.26	0.98
Error	187.03	135	2.49		
Total	3998.87	150			
Corrected Total	254.08	149			
R Squared = .264 (Adjusted R Squared = .126)					
Thickness swelling after 24 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	191.13	14	13.65	2.41	0.01
Intercept	7679.77	1	7679.77	1354.20	0.00
Tannin concentration (1)	138.93	2	69.47	12.25	0.00
Formulations (2)	34.61	4	8.65	1.53	0.20
(1) × (2)	17.59	8	2.20	0.39	0.92
Error	425.33	135	5.67		
Total	8296.22	150			
Corrected Total	616.46	149			
R Squared = .310 (Adjusted R Squared = .181)					

Table C.4 Result of Duncan test for thickness swelling after 2 and 24 hours for poplar plywoods with treated glueline

Thickness swelling after 2 hours		
	Subset	
Formulations	a	b
Tannin/Hexamine + PMDI + BA 4%	5.50	
Tannin/Hexamine + PMDI + BA 3%	6.30	6.30
Tannin/Hexamine + PMDI + BA 2%	6.52	6.52
Tannin/Hexamine		6.80
Tannin/Hexamine + PMDI		7.14
Sig.	0.07	0.15
Thickness swelling after 24 hours		
Formulations	Subset	
	a	b
Tannin/Hexamine + PMDI + BA 4%	8.22	
Tannin/Hexamine + PMDI	9.04	9.04
Tannin/Hexamine + PMDI + BA 2%	9.32	9.32
Tannin/Hexamine + PMDI + BA 3%	9.48	9.48
Tannin/Hexamine		10.12
Sig.	0.15	0.22

Table C.5 Result of ANOVA test for swelling parallel to the board surface grain for poplar plywoods with treated glueline after 2 and 24 hours soaking in water hours

Swelling parallel to the board surface grain after 2 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	4.19	14	0.30	2.21	0.01
Intercept	19.70	1	19.70	145.46	0.00
Tannin concentration (1)	2.19	2	1.09	8.08	0.00
Formulations (2)	0.84	4	0.21	1.55	0.20
(1) × (2)	1.16	8	0.15	1.07	0.39
Error	10.16	135	0.14		
Total	34.05	150			
Corrected Total	14.35	149			
R Squared = .292 (Adjusted R Squared = .160)					
Swelling parallel to the board surface grain after 24 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	20.32	14	1.45	2.84	0.00
Intercept	43.37	1	43.37	84.80	0.00
Tannin concentration (1)	6.14	2	3.07	6.00	0.00
Formulations (2)	5.92	4	1.48	2.89	0.03
(1) × (2)	8.26	8	1.03	2.02	0.06
Error	38.36	135	0.51		
Total	102.05	150			
Corrected Total	58.68	149			
R Squared = .346 (Adjusted R Squared = .224)					

Table C.6 Result of Duncan test for swelling parallel to the board surface grain for poplar plywoods with treated glueline after 2 and 24 hours soaking in water hours

Swelling parallel to the board surface grain after 2 hours		
	Subset	
Formulations	a	b
Tannin/Hexamine + PMDI + BA 4%	0.35	
Tannin/Hexamine + PMDI + BA 2%	0.41	0.41
Tannin/Hexamine + PMDI	0.44	0.44
Tannin/Hexamine + PMDI + BA 3%	0.51	0.51
Tannin/Hexamine		0.63
Sig.	0.26	0.09
Swelling parallel to the board surface grain after 24 hours		
	Subset	
Formulations	a	b
Tannin/Hexamine + PMDI + BA 4%	0.35	
Tannin/Hexamine + PMDI + BA 2%	0.41	0.41
Tannin/Hexamine + PMDI	0.44	0.44
Tannin/Hexamine + PMDI + BA 3%	0.51	0.51
Tannin/Hexamine		0.63
Sig.	0.26	0.09

Table C.7 Result of two-way AVOVA for swelling parallel to the board surface grain for poplar plywoods with treated glueline after 2 and 24 hours soaking

Swelling parallel to the board surface grain after 2 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	22.961(a)	14.00	1.64	4.14	0.00
Intercept	117.85	1.00	117.85	297.56	0.00
Tannin concentration (1)	8.75	2.00	4.37	11.04	0.00
Formulations (2)	10.58	4.00	2.65	6.68	0.00
(1) × (2)	3.63	8.00	0.45	1.15	0.34
Error	29.70	75.00	0.40		
Total	170.51	90			
Corrected Total	52.67	89			
a	R Squared = .436 (Adjusted R Squared = .331)				
Swelling parallel to the board surface grain after 24 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	68.00	14	4.86	6.95	0.00
Intercept	278.71	1	278.71	398.90	0.00
Tannin concentration (1)	33.32	2	16.66	23.84	0.00
Formulations (2)	26.67	4	6.67	9.54	0.00
(1) × (2)	8.01	8	1.00	1.43	0.20
Error	52.40	75	0.70		
Total	399.11	90			
Corrected Total	120.40	89			
a	R Squared = .565 (Adjusted R Squared = .484)				

Table C.8 Result of Duncan test for swelling parallel to the board surface grain for poplar plywoods with treated glueline after 2 and 24 hours soaking

Swelling parallel to the board surface grain after 2 hours			
	Subset		
Formulations	a	b	c
Tannin/Hexamine + PMDI + BA 4%	0.67		
Tannin/Hexamine + PMDI + BA 2%	1.02	1.02	
Tannin/Hexamine + PMDI + BA 3%	1.03	1.03	
Tannin/Hexamine + PMDI		1.29	
Tannin/Hexamine			1.71
Sig.	0.12	0.24	1.00
Swelling parallel to the board surface grain after 24 hours			
	Subset		
Formulations	a	b	c
Tannin/Hexamine + PMDI + BA 4%	1.20		
Tannin/Hexamine + PMDI + BA 2%	1.40	1.40	
Tannin/Hexamine + PMDI + BA 3%	1.51	1.51	
Tannin/Hexamine + PMDI		1.97	
Tannin/Hexamine			2.72
Sig.	0.29	0.05	1.00

Table C.9 Result of two-way ANOVA for tensile shear strength of poplar plywoods with treated glueline before and after soaking in water

Tensile shear strength before soaking					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	7.031(a)	14	0.502	24.006	0
Intercept	115.24	1	115.238	5508.49	0
Tannin concentration (1)	1.52	2	0.758	36.227	0
Formulations (2)	4.76	4	1.19	56.9	0
(1) × (2)	0.75	8	0.094	4.503	0
Error	1.57	135	0.021		
Total	123.84	150			
Corrected Total	8.60	149			
R Squared = .818 (Adjusted R Squared = .783)					
Tensile shear strength after soaking					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	2.83	14	0.20	11.20	0.00
Intercept	55.35	1	55.35	3063.22	0.00
Tannin concentration (1)	0.58	2	0.29	16.08	0.00
Formulations (2)	2.07	4	0.52	28.63	0.00
(1) × (2)	0.18	8	0.02	1.27	0.27
Error	1.36	135	0.02		
Total	59.54	150			
Corrected Total	4.19	149			
R Squared = .677 (Adjusted R Squared = .616)					

Table C.10 Result of Duncan for tensile shear strength of poplar plywoods with treated glueline before and after soaking in water

Tensile shear strength before soaking				
	Subset			
Formulations	a	b	c	d
Tannin/Hexamine	0.78			
Tannin/Hexamine + PMDI		0.96		
Tannin/Hexamine + PMDI + BA 2%			1.26	
Tannin/Hexamine + PMDI + BA 3%			1.27	
Tannin/Hexamine + PMDI + BA 4%				1.4
Sig.	1	1	0.90	1

Tensile shear strength after soaking			
	Subset		
Formulations	a	b	c
Tannin/Hexamine	0.52		
Tannin/Hexamine + PMDI		0.70	
Tannin/Hexamine + PMDI + BA 2%			0.88
Tannin/Hexamine + PMDI + BA 3%			0.89
Tannin/Hexamine + PMDI + BA 4%			0.93
Sig.	1	1	0.23

Table C.11 Result of two-way ANOVA test for density of beech plywoods with treated glueline

Dry Density					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	1367.98	9	152.00	0.54	0.83
Intercept	22245271.84	1	22245271.84	79681.43	0.00
Tannin concentration (1)	8.27	1	8.27	0.03	0.86
Formulations (2)	1071.77	4	267.94	0.96	0.44
(1) × (2)	322.30	4	80.58	0.29	0.88
Error	13679.70	90	279.18		
Total	22823548.71	100			
Corrected Total	15047.68	99			
R Squared = .091 (Adjusted R Squared = -.076)					
Conditioning Density					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	3621.42	9	402.38	0.84	0.58
Intercept	59886452.58	1	59886452.58	125722.41	0.00
Tannin concentration (1)	0.33	1	0.33	0.00	0.98
Formulations (2)	3093.86	4	773.47	1.62	0.17
(1) × (2)	361.37	4	90.34	0.19	0.94
Error	65258.40	137	476.34		
Total	61941540.76	147			
Corrected Total	68879.83	146			
R Squared = .053 (Adjusted R Squared = -.010)					

Table C.12 Result of two-way ANOVA test for water absorption of beech plywoods with treated glueline after 2 and 24 hours soaking

Water absorption after 2 hours soaking					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	313.63	9	34.85	2.90	0.01
Intercept	61259.70	1	61259.70	5100.62	0.00
Tannin concentration (1)	64.13	1	64.13	5.34	0.02
Formulations (2)	165.05	4	41.26	3.44	0.01
(1) × (2)	68.84	4	17.21	1.43	0.23
Error	936.80	90	12.01		
Total	64557.28	100			
Corrected Total	1250.43	99			
R Squared = .251 (Adjusted R Squared = .164)					
Water absorption after 24 hours soaking					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	2229.29	9	247.70	11.97	0.00
Intercept	203271.43	1	203271.43	9827.07	0.00
Tannin concentration (1)	2.50	1	2.50	0.12	0.73
Formulations (2)	2082.69	4	520.67	25.17	0.00
(1) × (2)	141.68	4	35.42	1.71	0.16
Error	1613.42	90	20.68		
Total	212292.98	100			
Corrected Total	3842.71	99			
R Squared = .580 (Adjusted R Squared = .532)					

Table C.13 Result of Duncan test for water absorption of beech plywoods with treated glueline after 2 and 24 hours soaking

Water absorption after 2 hours soaking		
Formulations	Subset	
	a	b
Tannin/Hexamine + PMDI + BA 5%	25.44	
Tannin/Hexamine	26.18	
Tannin/Hexamine + PMDI + BA 10%	26.41	
Tannin/Hexamine + BA 5%	27.10	
Tannin/Hexamine + BA 10%		29.66
Sig.	0.21	1.00
Water absorption after 24 hours soaking		
Formulations	Subset	
	a	b
Tannin/Hexamine + BA 5%	45.75	
Tannin/Hexamine	45.77	
Tannin/Hexamine + PMDI + BA 5%	45.99	
Tannin/Hexamine + PMDI + BA 10%	49.05	
Tannin/Hexamine + BA 10%		59.47
Sig.	0.06	1.00

Table C.14 Result of two-way ANOVA test for thickness swelling of beech plywoods with treated glueline after 2 and 24 hours soaking

Thickness swelling after 2 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	22.21	9	2.47	1.77	0.09
Intercept	2716.04	1	2716.04	1944.92	0.00
Tannin concentration (1)	4.02	1	4.02	2.88	0.09
Formulations (2)	17.03	4	4.26	3.05	0.02
(1) × (2)	0.73	4	0.18	0.13	0.97
Error	108.93	90	1.40		
Total	2911.24	100			
Corrected Total	131.14	99			
R Squared = .169 (Adjusted R Squared = .074)					
Thickness swelling after 24 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	192.03	9	21.34	8.33	0.00
Intercept	6971.51	1	6971.51	2720.70	0.00
Tannin concentration (1)	4.41	1	4.41	1.72	0.19
Formulations (2)	182.78	4	45.69	17.83	0.00
(1) × (2)	8.31	4	2.08	0.81	0.52
Error	199.87	90	2.56		
Total	7448.20	100			
Corrected Total	391.90	99			
R Squared = .490 (Adjusted R Squared = .431)					

Table C.15 Result of Duncan test for thickness swelling of beech plywoods with treated glueline after 2 and 24 hours soaking

Thickness swelling after 2 hours		
Formulations	Subset	
	a	b
Tannin/Hexamine + PMDI + BA 5%	4.89	
Tannin/Hexamine + BA 5%	5.65	5.65
Tannin/Hexamine + PMDI + BA 10%		5.76
Tannin/Hexamine + BA 10%		5.90
Tannin/Hexamine		6.22
Sig.	0.06	0.21

Thickness swelling after 24 hours			
Formulations	Subset		
	a	b	c
Tannin/Hexamine + PMDI + BA 5%	7.73		
Tannin/Hexamine + BA 5%	8.06		
Tannin/Hexamine	8.17		
Tannin/Hexamine + PMDI + BA 10%		9.91	
Tannin/Hexamine + BA 10%			11.70
Sig.	0.46	1	1

Table C.16 Result of two-way ANOVA test for swelling parallel to the board surface grain of beech plywoods with treated glueline after 2 and 24 hours soaking

Swelling parallel to the board surface grain after 2 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	2.15	9	0.24	2.95	0.00
Intercept	27.65	1	27.65	342.40	0.00
Tannin concentration (1)	0.12	1	0.12	1.48	0.23
Formulations (2)	1.74	4	0.43	5.39	0.00
(1) × (2)	0.23	4	0.06	0.72	0.58
Error	6.30	90	0.08		
Total	35.61	100			
Corrected Total	8.44	99			
R Squared = .254 (Adjusted R Squared = .168)					

Swelling parallel to the board surface grain after 22 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	412.12	9	45.79	24.61	0.00
Intercept	575.75	1	575.75	309.38	0.00
Tannin concentration (1)	1.18	1	1.18	0.63	0.43
Formulations (2)	411.19	4	102.80	55.24	0.00
(1) × (2)	5.68	4	1.42	0.76	0.55
Error	145.15	90	1.86		
Total	1051.74	100			
Corrected Total	557.28	99			
R Squared = .740 (Adjusted R Squared = .709)					

Table C.17 Result of Duncan test for swelling parallel to the board surface grain of beech plywoods with treated glueline after 2 and 24 hours soaking

Swelling parallel to the board surface grain after 2 hours		
Formulations	Subset	
	a	b
Tannin/Hexamine + BA 5%	0.43	
Tannin/Hexamine + PMDI + BA 5%	0.46	
Tannin/Hexamine + PMDI + BA 10%	0.56	
Tannin/Hexamine	0.58	
Tannin/Hexamine + BA 10%		0.85
Sig.	0.17	1.00

Swelling parallel to the board surface grain after 24 hours			
Formulations	Subset		
	a	b	c
Tannin/Hexamine + PMDI + BA 5%	0.87		
Tannin/Hexamine + BA 5%	1.01		
Tannin/Hexamine	1.03		
Tannin/Hexamine + PMDI + BA 10%		3.26	
Tannin/Hexamine + BA 10%			6.85
Sig.	0.75	1.00	1.00

Table C.18 Result of two-way ANOVA test for swelling perpendicular to the board surface grain of beech plywoods with treated glueline after 2 and 24 hours soaking

Swelling perpendicular to the board surface grain after 2 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	4.00	9	0.44	3.53	0.00
Intercept	74.78	1	74.78	594.13	0.00
Tannin concentration (1)	0.09	1	0.09	0.70	0.41
Formulations (2)	3.33	4	0.83	6.62	0.00
(1) × (2)	0.33	4	0.08	0.66	0.62
Error	9.82	90	0.13		
Total	87.77	100			
Corrected Total	13.82	99			
a	R Squared = .290 (Adjusted R Squared = .208)				

Swelling perpendicular to the board surface grain after 24 hours					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	359.75	9	39.97	28.34	0.00
Intercept	868.01	1	868.01	615.34	0.00
Tannin concentration (1)	0.06	1	0.06	0.04	0.84
Formulations (2)	341.76	4	85.44	60.57	0.00
(1) × (2)	18.83	4	4.71	3.34	0.01
Error	110.03	90	1.41		
Total	1259.79	100			
Corrected Total	469.78	99			
a	R Squared = .766 (Adjusted R Squared = .739)				

Table C.19 Result of Duncan test for swelling perpendicular to the board surface grain of beech plywoods with treated glueline after 2 and 24 hours soaking

Swelling perpendicular to the board surface grain after 2 hours			
Formulations	Subset		
	a	b	c
Tannin/Hexamine + PMDI + BA 5%	0.72		
Tannin/Hexamine + BA 5%	0.77	0.77	
Tannin/Hexamine + PMDI + BA 10%	0.95	0.95	
Tannin/Hexamine		0.99	
Tannin/Hexamine + BA 10%			1.31
Sig.	0.09	0.10	1.00
Swelling perpendicular to the board surface grain after 24 hours			
Formulations	Subset		
	a	b	c
Tannin/Hexamine + PMDI + BA 5%	1.47		
Tannin/Hexamine + BA 5%	1.72		
Tannin/Hexamine	1.85		
Tannin/Hexamine + PMDI + BA 10%		4.09	
Tannin/Hexamine + BA 10%			6.94
Sig.	0.38	1.00	1.00

Table C.20 Result of two-way ANOVA for tensile shear of beech plywoods with treated glueline before and after 24 hours soaking

Tensile shear before soaking					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	9.85	9	1.10	23.08	0.00
Intercept	209.12	1	209.12	4405.02	0.00
Tannin concentration (1)	0.27	1	0.27	5.60	0.02
Formulations (2)	9.04	4	2.26	47.61	0.00
(1) × (2)	0.55	4	0.14	2.91	0.03
Error	3.80	90	0.05		
Total	222.78	100			
Corrected Total	13.66	99			
R Squared = .722 (Adjusted R Squared = .691)					
Tensile shear after 24 hours soaking					
Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	1.88	9	0.21	7.15	0.00
Intercept	76.33	1	76.33	2608.56	0.00
Tannin concentration (1)	0.05	1	0.05	1.67	0.20
Formulations (2)	1.42	4	0.36	12.16	0.00
(1) × (2)	0.41	4	0.10	3.50	0.01
Error	2.34	90	0.03		
Total	80.56	100			
Corrected Total	4.22	99			
R Squared = .446 (Adjusted R Squared = .383)					

Table C.21 Result of Duncan test for tensile shear of beech plywoods with treated glueline before and after 24 hours soaking

Tensile shear before soaking				
Formulations	Subset			
	a	b	c	d
Tannin/Hexamine	1.01			
Tannin/Hexamine + BA 5%		1.32		
Tannin/Hexamine + PMDI + BA 5%			1.63	
Tannin/Hexamine + BA 10%				1.81
Tannin/Hexamine + PMDI + BA 10%				1.85
Sig.	1.00	1.00	1.00	0.59
Tensile shear after soaking				
Formulations	Subset			
	a	b	c	d
Tannin/Hexamine	0.74			
Tannin/Hexamine + BA 10%	0.84	0.84		
Tannin/Hexamine + BA 5%		0.94	0.94	
Tannin/Hexamine + PMDI + BA 10%			0.96	
Tannin/Hexamine + PMDI + BA 5%				1.12
Sig.	0.09	0.10	0.62	1.00

Table C.22 Result of ANOVA for density of beech plywoods with treated veneers

Conditioning density					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	182010.1	9.00	20223.34	40.79	0.00
Within Groups	72377.64	146.00	495.74		
Total	254387.7	155			
Dry density					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	58820.2	9	6535.57	11.63	0.00
Within Groups	34251.94	91	561.50		
Total	93072.14	100			

Table C.23 Result of Duncan test for density of beech plywoods with treated veneers

Conditioning Density				
Treatments	Subset for alpha = .05			
	a	b	c	d
Treated with water	651.86			
0.5% BA	652.26			
Control	655.52			
0.5% BA-non treated core layer	657.13			
1% BA	658.55			
1% BA-non treated core layer	659.04			
10% Tan.+ 0.5% BA–non treated core layer		690.86		
10% Tan.+ 0.5% BA			721.16	
20% Tan.+ 1% BA–non treated core layer			732.48	732.48
20% Tan.+ 1% BA				738.41
Sig.	0.44	1.00	0.16	0.46
Oven dry Density				
Treatments	Subset for alpha = .05			
	a	b	c	d
1% BA-non treated core layer	618.26			
Treated with water	618.80			
0.5% BA	619.75			
0.5% BA-non treated core layer	620.05			
1% BA	621.69			
Control	622.97			
10% Tan.+ 0.5% BA–non treated core layer		651.79		
10% Tan.+ 0.5% BA		660.14	660.14	
20% Tan.+ 1% BA–non treated core layer			683.96	683.96
20% Tan.+ 1% BA				693.31
Sig.	0.76	0.52	0.07	0.47

Table C.24 Result of ANOVA test for water absorption of beech plywoods with treated veneers after 2 and 24 hours soaking in water

Water absorption after 2 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	349.89	9	38.88	2.15	0.03
Within Groups	1446.51	81	18.08		
Total	1796.40	99			
Water absorption after 24 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	171.78	9	19.09	1.89	0.06
Within Groups	807.09	81	10.09		
Total	978.87	99			

Table C.25 Result of Duncan test for water absorption of beech plywoods with treated veneers after 2 and 24 hours soaking in water

Water absorption after 2 hours			
Treatments	Subset for alpha = .05		
	2	1	
20% Tan.+ 1% BA	21.80		
20% Tan.+ 1% BA–non treated core layer	25.75	25.75	
1% BA		27.40	
10% Tan.+ 0.5% BA–non treated core layer		27.78	
Treated with water		28.27	
Control		28.45	
0.5% BA		28.46	
10% Tan.+ 0.5% BA		28.47	
0.5% BA-non treated core layer		28.67	
1% BA-non treated core layer		29.16	
Sig.	0.06	0.17	
Water absorption after 24 hours			
Treatments	Subset for alpha = .05		
	a	b	c
20% Tan.+ 1% BA	40.27		
20% Tan.+ 1% BA–non treated core layer	40.77	40.77	
1% BA-non treated core layer	43.02	43.02	43.02
0.5% BA	43.46	43.46	43.46
1% BA	43.69	43.69	43.69
10% Tan.+ 0.5% BA–non treated core layer		43.82	43.82
Treated with water		44.06	44.06
0.5% BA-non treated core layer		44.08	44.08
Control			44.40
10% Tan.+ 0.5% BA			44.52
Sig.	0.05	0.07	0.42

Table C.26 Result of ANOVA test for thickness swelling of beech plywoods with treated veneers after 2 and 24 hours soaking in water

Thickness swelling after 2 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	9.39	9	1.04	0.58	0.81
Within Groups	145.09	81	1.81		
Total	154.48	99			
Thickness swelling after 2 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	6.28	9	0.70	0.25	0.99
Within Groups	225.31	81	2.82		
Total	231.59	99			

Table C.27 Result of ANOVA test for swelling parallel to the board surface grain of beech plywoods with treated veneers after 2 and 24 hours soaking in water

Swelling parallel to the board surface grain after 2 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.110085	9	0.012232	0.403743	0.929631
Within Groups	2.423648	80	0.030296		
Total	2.533733	89			
Swelling parallel to the board surface grain after 24 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Total	231.5947	89			
Between Groups	0.177811	9	0.019757	0.645173	0.755166
Within Groups	2.449793	80	0.030622		

Table C.28 Result of ANOVA test for swelling perpendicular to the board surface grain of beech plywoods with treated veneers after 2 and 24 hours soaking in water

Swelling perpendicular to the board surface grain after 2 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.15	9	0.02	0.57	0.82
Within Groups	2.33	81	0.03		
Total	2.48	99			
Swelling perpendicular to the board surface grain after 24 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.17	9	0.02	0.66	0.74
Within Groups	2.29	81	0.03		
Total	2.47	99			

Table C.29 Result of ANOVA test for tensile shear strength of beech plywoods with treated veneers after different pre-treatment

Air dried conditioned					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1.18	9.00	0.13	2.43	0.02
Within Groups	3.78	70.00	0.05		
Total	4.96	79.00			
After 24 hours soaking in cold water					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1.97	9.00	0.22	4.29	0.00
Within Groups	3.57	70.00	0.05		
Total	5.53	79.00			
After 6 hours boiling					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.53	9.00	0.06	1.25	0.28
Within Groups	3.31	70.00	0.05		
Total	3.85	79.00			

Table C.30 Result of Duncan test for tensile shear strength of beech plywoods with treated veneers after different pre-treatment

Air dried conditioned

Treatments	Subset for alpha = .05		
	a	b	c
20% Tan.+ 1% BA	1.90		
20% Tan.+ 1% BA–non treated core layer	1.93	1.93	
10% Tan.+ 0.5% BA	1.97	1.97	
10% Tan.+ 0.5% BA–non treated core layer	2.00	2.00	2.00
1% BA	2.14	2.14	2.14
1% BA-non treated core layer		2.17	2.17
0.5% BA		2.18	2.18
Treated with water		2.18	2.18
Control		2.20	2.20
0.5% BA-non treated core layer			2.26
Sig.	0.07	0.06	0.06

After 24 hours soaking in cold water

Treatments	Subset for alpha = .05				
	a	b	c	d	e
20% Tan.+ 1% BA	1.67				
20% Tan.+ 1% BA–non treated core layer		1.92			
Treated with water		1.93	1.93		
10% Tan.+ 0.5% BA		1.93	1.93		
10% Tan.+ 0.5% BA–non treated core layer		1.95	1.95	1.95	
0.5% BA		2.02	2.02	2.02	2.02
Control		2.07	2.07	2.07	2.07
1% BA			2.18	2.18	2.18
1% BA-non treated core layer				2.20	2.20
0.5% BA-non treated core layer					2.20
Sig.	1.00	0.26	0.05	0.05	0.15

After 6 hours boiling

Treatments	Subset for alpha = .05
20% Tan.+ 1% BA	1.35
10% Tan.+ 0.5% BA	1.37
20% Tan.+ 1% BA–non treated core layer	1.38
10% Tan.+ 0.5% BA–non treated core layer	1.47
Treated with water	1.49
0.5% BA-non treated core layer	1.50
Control	1.52
1% BA	1.54
1% BA-non treated core layer	1.58
0.5% BA	1.59
Sig.	0.06

Table C.31 Result of ANOVA test for density of poplar plywoods with treated veneers

Oven dry Density					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.01	4.00	0.00	2.62	0.04
Within Groups	0.04	55.00	0.00		
Total	0.05	59.00			
Conditioning Density					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.00	4.00	0.00	1.63	0.20
Within Groups	0.01	25.00	0.00		
Total	0.02	29.00			

Table C.32 Result of ANOVA test for density of poplar plywoods with treated veneers

Treatments	Subset for alpha = .05	
	2	1
Treated with water	0.48	
Control	0.48	
1% BA	0.48	
10% Tan.+1% BA- non treated core layer	0.49	0.49
10% Tan.+1% BA		0.51
Sig.	0.37	0.07

Table C.33 Result of ANOVA test for water absorption of poplar plywoods with treated veneers after 2 and 24 hours soaking in water

water absorption after 24 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	15.01	4.00	3.75	0.11	0.98
Within Groups	816.10	25.00	32.64		
Total	831.11	29.00			
water absorption after 24 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	37.77	4.00	9.44	0.30	0.87
Within Groups	779.13	25.00	31.17		
Total	816.90	29.00			

Table C.34 Result of ANOVA test for thickness swelling of poplar plywoods with treated veneers after 2 and 24 hours soaking in water

Thickness swelling after 2 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2.57	4.00	0.64	0.47	0.75
Within Groups	33.83	25.00	1.35		
Total	36.40	29.00			
Thickness swelling after 24 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.19	4.00	0.05	0.02	1.00
Within Groups	66.07	25.00	2.64		
Total	66.26	29.00			

Table C.35 Result of ANOVA test for swelling parallel to the board surface grain of poplar plywoods with treated veneers after 2 and 24 hours soaking in water

Swelling parallel to the board surface grain after 2 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.01	4.00	0.00	0.23	0.92
Within Groups	0.27	25.00	0.01		
Total	0.28	29.00			
Swelling parallel to the board surface grain after 24 hours					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.10	4.00	0.03	2.06	0.12
Within Groups	0.31	25.00	0.01		
Total	0.42	29.00			

Table C.36 Result of ANOVA test for swelling perpendicular to the board surface grain of poplar plywoods with treated veneers after 2 and 24 hours soaking in water

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.09	4.00	0.02	0.64	0.64
Within Groups	0.90	25.00	0.04		
Total	0.99	29.00			
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.08	4.00	0.02	0.47	0.76
Within Groups	1.08	25.00	0.04		
Total	1.17	29.00			

Table C.37 Result of one-way ANOVA test for tensile shear strength of poplar plywoods with treated veneers after three pre-treatment prior testing

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.05	4.00	0.01	0.27	0.89
Within Groups	1.25	30.00	0.04		
Total	1.29	34.00			
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.16	4.00	0.04	1.39	0.26
Within Groups	0.87	30.00	0.03		
Total	1.03	34.00			
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	0.01	4.00	0.00	0.18	0.95
Within Groups	0.28	30.00	0.01		
Total	0.29	34.00			

C.2: Statistical analysis for fungal test

Table C.38 Result of one-way ANOVA test for weight loss of poplar plywoods with treated gluelines after fungal test before leaching

Tannin 40%						
		Sum of Squares	df	Mean Square	F	Sig.
dry	Between Groups	2407.83	4	601.96	66.42	0.00
	Within Groups	90.63	10	9.06		
	Total	2498.46	14			
Tannin 45%						
		Sum of Squares	df	Mean Square	F	Sig.
wet	Between Groups	2330.33	4	582.58	78.79	0.00
	Within Groups	73.94	10	7.39		
	Total	2404.27	14			
Tannin 50%						
		Sum of Squares	df	Mean Square	F	Sig.
bioled	Between Groups	3424.29	4	856.07	118.09	0.00
	Within Groups	72.49	10	7.25		
	Total	3496.78	14			

Table C.39 Result of Duncan test for weight loss of poplar plywoods with treated gluelines after fungal test before leaching

Tannin 40%				
Formulations	Subset for alpha = .05			
	2	3	4	1
Tannin/hexamine + PMDI + Boric acid 4%	13.95			
Tannin/hexamine + PMDI + Boric acid 3%		27.89		
Tannin/hexamine + PMDI + Boric acid 2%			40.62	
Tannin/hexamine				46.35
Tannin/hexamine + PMDI				47.19
Sig.	1.00	1.00	1.00	0.74
Tannin 45%				
Formulations	Subset for alpha = .05			
	2	3	4	1
Tannin/hexamine + PMDI + Boric acid 4%	13.15			
Tannin/hexamine + PMDI + Boric acid 3%		30.96		
Tannin/hexamine + PMDI + Boric acid 2%			40.84	
Tannin/hexamine			43.50	43.50
Tannin/hexamine + PMDI				48.32
Sig.	1.00	1.00	0.26	0.06
Tannin 50%				
Formulations	Subset for alpha = .05			
	2	3	4	1
Tannin/hexamine + PMDI + Boric acid 4%	7.37			
Tannin/hexamine + PMDI + Boric acid 3%		18.23		
Tannin/hexamine + PMDI + Boric acid 2%			30.85	
Tannin/hexamine + PMDI				45.48
Tannin/hexamine				45.86
Sig.	1.00	1.00	1.00	0.87

Table C.40 Result of ANOVA test for weight loss of poplar plywoods with treated gluelines after fungal test leached by EN 1250-2

Tannin 45%					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	373.64	4.00	93.41	3.28	0.06
Within Groups	284.92	10.00	28.49		
Total	658.57	14.00			
Tannin 50%					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2179.32	4.00	544.83	18.12	0.00
Within Groups	300.63	10.00	30.06		
Total	2479.95	14.00			

Table C.41 Result of Duncan test for weight loss of poplar plywoods with treated gluelines after fungal test leached by EN 1250-2

Tannin 45%		
Formulations	Subset for alpha = .05	
	a	b
Tannin/hexamine + PMDI + Boric acid 4%	11.03	
Tannin/hexamine + PMDI + Boric acid 2%		36.59
Tannin/hexamine + PMDI + Boric acid 3%		37.06
Tannin/hexamine + PMDI		41.71
Tannin/hexamine		45.13
Sig.	1.00	0.11
Tannin 50%		
Formulations	Subset for alpha = .05	
	a	b
Tannin/hexamine + PMDI + Boric acid 4%	31.94	
Tannin/hexamine + PMDI + Boric acid 3%	36.75	36.75
Tannin/hexamine + PMDI + Boric acid 2%	38.97	38.97
Tannin/hexamine + PMDI		44.73
Tannin/hexamine		45.17
Sig.	0.15	0.10

Table C.42 Result of ANOVA test for weight loss of poplar plywoods with treated gluelines after fungal test leached by EN 84

Tannin 45%					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	39.62	4	9.90	0.20	0.93
Within Groups	492.23	10	49.22		
Total	531.84	14			
Tannin 50%					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	176.88	4	44.22	1.12	0.40
Within Groups	394.73	10	39.47		
Total	571.61	14			

Table C.43 Result of ANOVA test for weight loss of beech plywoods with treated gluelines after fungal test before leaching

Tannin 45%					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2588.28	4	647.07	34.82	0.00
Within Groups	185.81	10	18.58		
Total	2774.09	14			
Tannin 50%					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3827.94	4	956.98	68.54	0.00
Within Groups	139.64	10	13.96		
Total	3967.57	14			

Table C.44 Result of Duncan test for weight loss of beech plywoods with treated gluelines after fungal test before leaching

Tannin 45%		
Treatments	Subset for alpha = .05	
	a	b
Tannin/Hexamine +10% BA	13.37	
Tannin/Hexamine + PMDI +10% BA	13.54	
Tannin/Hexamine + PMDI +5% BA	14.40	
Tannin/Hexamine +5% BA	17.99	
Tannin/Hexamine		47.40
Sig.	0.25	1.00
Tannin 50%		
Treatments	Subset for alpha = .05	
	a	b
Tannin/Hexamine + PMDI +5% BA	9.87	
Tannin/Hexamine + PMDI +10% BA	12.68	
Tannin/Hexamine +5% BA	12.93	
Tannin/Hexamine +10% BA	13.31	
Tannin/Hexamine		52.02
Sig.	0.32	1.00

Table C.45 Result of ANOVA test for weight loss of beech plywoods with treated gluelines after fungal test leached by EN 1250-2

Tannin 45%					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1677.57	4	419.39	16.51	0.00
Within Groups	254.07	10	25.41		
Total	1931.64	14			
Tannin 50%					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2518.57	4	629.64	37.55	0.00
Within Groups	167.66	10	16.77		
Total	2686.23	14			

Table C.46 Result of Duncan test for weight loss of beech plywoods with treated gluelines after fungal test leached by EN 1250-2

Tannin 45%		
Treatments	Subset for alpha = .05	
	a	b
Tannin/Hexamine + PMDI +5% BA	19.07	
Tannin/Hexamine + PMDI +10% BA	20.91	
Tannin/Hexamine +10% BA	23.82	
Tannin/Hexamine +5% BA	24.65	
Tannin/Hexamine		48.07
Sig.	0.23	1

Tannin 50%			
Treatments	Subset for alpha = .05		
	a	b	c
Tannin/Hexamine + PMDI +5% BA	15.98		
Tannin/Hexamine +5% BA	18.83	18.83	
Tannin/Hexamine + PMDI +10% BA	19.02	19.02	
Tannin/Hexamine +10% BA		24.90	
Tannin/Hexamine			51.25
Sig.	0.41	0.11	1

Table C.47 Result of ANOVA test for weight loss of beech plywoods with treated gluelines after fungal test leached by EN 84

Tannin 45%					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1354.07	4	338.52	29.44	0.00
Within Groups	114.99	10	11.50		
Total	1469.06	14			
Tannin 50%					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	659.49	4	164.87	9.16	0.00
Within Groups	180.08	10	18.01		
Total	839.57	14			

Table C.48 Result of Duncan test for weight loss of beech plywoods with treated glueline after fungal test leached by EN 84

Tannin 45%		
Treatments	Subset for alpha = .05	
	a	b
Tannin/Hexamine + PMDI +10% BA	27.72	
Tannin/Hexamine +10% BA	29.21	
Tannin/Hexamine +5% BA		46.60
Tannin/Hexamine + PMDI +5% BA		48.32
Tannin/Hexamine		48.44
Sig.	0.60	0.54
Tannin 50%		
Treatments	Subset for alpha = .05	
	a	b
Tannin/Hexamine + PMDI +10% BA	27.53	
Tannin/Hexamine +10% BA	27.62	
Tannin/Hexamine +5% BA		38.63
Tannin/Hexamine + PMDI +5% BA		40.13
Tannin/Hexamine		43.44
Sig.	0.98	0.22

Table C.49 Result of ANOVA test for weight loss of beech plywoods with treated veneers after fungal test before leaching

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	6923.297	9	769.26	126.56	0.00
Within Groups	121.566	20	6.08		
Total	7044.863	29			

Table C.50 Result of Duncan test for weight loss of beech plywoods with treated veneers after fungal test before leaching

	Subset for alpha = .05		
Treatments	a	b	c
1% BA	0.65		
1% BA-non treated core layer	0.76		
0.5% BA	0.8		
0.5% BA-non treated core layer	0.85		
20% Tan.+ 1% BA	0.88		
20% Tan.+ 1% BA–non treated core layer	1.07		
10% Tan.+ 0.5% BA	1.64		
10% Tan.+ 0.5% BA–non treated core layer	5.26		
Treated with water		35.99	
Control			42.33
Sig.	0.06	1	1

Table C.51 Result of ANOVA test for weight loss of beech plywoods with treated veneers after fungal test leached by EN 1250-2

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	4337.09	9	481.90	48.71	0.00
Within Groups	197.86	20	9.89		
Total	4534.95	29			

Table C.52 Result of ANOVA test for weight loss of beech plywoods with treated veneers after fungal test leached by EN 1250-2

Treatments	Subset for alpha = .05			
	a	b	c	d
20% Tan.+ 1% BA	5.59			
10% Tan.+ 0.5% BA		11.82		
20% Tan.+ 1% BA–non treated core layer		15.33		
1% BA			23.32	
10% Tan.+ 0.5% BA–non treated core layer			24.92	
0.5% BA			26.21	
1% BA-non treated core layer				37.64
0.5% BA-non treated core layer				38.95
Treated with water				38.96
Control				41.37
Sig.	1.00	0.19	0.30	0.20

Table C.53 Result of ANOVA test for weight loss of beech plywoods with treated veneers after fungal test leached by EN 84

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2537.58	9	281.95	15.68	0.00
Within Groups	359.59	20	17.98		
Total	2897.17	29			

Table C.54 Result of Duncan test for weight loss of beech plywoods with treated veneers after fungal test leached by EN 84

	Subset for alpha = .05		
Treatments	a	b	c
20% Tan.+ 1% BA	18.76		
20% Tan.+ 1% BA–non treated core layer		29.58	
10% Tan.+ 0.5% BA		33.75	
Treated with water			41.19
10% Tan.+ 0.5% BA–non treated core layer			42.64
1% BA-non treated core layer			44.93
0.5% BA-non treated core layer			45.73
Control			47.09
1% BA			47.13
0.5% BA			48.99
Sig.	1	0.24	0.06

Table C.55 Result of ANOVA test for weight loss of poplar plywoods with treated veneers after fungal test before and after leaching

Not leached					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5638.06	4	1409.52	272.95	0.00
Within Groups	51.64	10	5.16		
Total	5689.70	14			
Leached by EN 1250-2					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	4981.01	4	1245.25	77.09	0.00
Within Groups	161.53	10	16.15		
Total	5142.54	14			
Leached by EN 84					
	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	33.63	4	8.41	0.47	0.76
Within Groups	177.51	10	17.75		
Total	211.14	14			

Table C.56 Result of Duncan test for weight loss of poplar plywoods with treated veneers after fungal test before and after leaching

Not leached				
Treatments	Subset for alpha = .05			
	a	b		
BA 1%	0.36			
Tannin 10% + BA 1%	0.51			
Tannin 10%+ BA 1%- Non treated core layer	0.75			
Treated with water		39.78		
Control		40.44		
Sig.	0.85	0.73		
Leached by EN 1250-2				
Treatments	Subset for alpha = .05			
	a	b	c	d
Tannin 10% + BA 1%	4.51			
Tannin 10%+ BA 1%- Non treated core layer		27.90		
BA 1%			44.66	
Treated with water			49.20	49.20
Control				54.82
Sig.	1	1	0.20	0.12
Leached by EN 84				
Treatments	Subset for alpha = .05			
Tannin 10% + BA 1%	41.65			
Tannin 10%+ BA 1%- Non treated core layer	43.81			
BA 1%	44.51			
Treated with water	45.23			
Control	46.05			
Sig.	0.27			

Annex D. Results of Fungal test and moisture content at the end of the test

Table D.1 Fungal test results of poplar plywoods with treated tannin glue before leaching

	Formulations	Total retention of boric acid kg/m^3	Humidity Average at the end of the test (Std. dev.) %	Average weight loss (Std. dev.) %
Tannin 40 %	Tannin/Hexamine	0	174.39 (17.18)	46.35 **a** (3.25)
	Tannin/Hexamine + PMDI	0	199.64 (29.84)	47.19 **a** (2.07)
	Tannin/Hexamine + PMDI + BA 2%	0.343	123.08 (46.06)	40.62 **b** (1.75)
	Tannin/Hexamine + PMDI + BA 3%	0.513	122.74 (33.12)	27.89 **c** (4.22)
	Tannin/Hexamine + PMDI + BA 4%	0.684	101.60 (6.37)	13.95 **d** (3.10)
Tannin 45 %	Tannin/Hexamine	0	113.47 (11.13)	43.50 **a** (1.01)
	Tannin/Hexamine + PMDI	0	132.64 (44.02)	48.32 **ab** (2.30)
	Tannin/Hexamine + PMDI + BA 2%	0.373	102.46 (32.12)	40.84 **b** (3.86)
	Tannin/Hexamine + PMDI + BA 3%	0.560	116.17 (22.20)	30.96 **c** (3.45)
	Tannin/Hexamine + PMDI + BA 4%	0.746	117.00 (8.86)	13.15 **d** (1.96)
Tannin 50 %	Tannin/Hexamine	0	139.40 (24.30)	45.86 **a** (0.88)
	Tannin/Hexamine + PMDI	0	144.06 (21.02)	45.48 **a** (3.29)
	Tannin/Hexamine + PMDI + BA 2%	0.377	138.62 (28.44)	30.85 **b** (2.82)
	Tannin/Hexamine + PMDI + BA 3%	0.607	120.42 (21.98)	18.23 **c** (3.29)
	Tannin/Hexamine + PMDI + BA 4%	0.811	131.35 (27.20)	7.37 **d** (2.43)

Table D.2 Fungal test results of poplar plywoods with treated tannin glue after EN 1250-2 leaching test

	Formulations	Weight loss after leaching kg/m^3	Humidity Average at the end of the test (Std. dev.) %	Average weight loss (Std. dev.) %
Tannin 45 %	Tannin/Hexamine	2.01 (0.38)	179.87 (54.81)	45.17 **a** (6.05)
	Tannin/Hexamine + PMDI	2.18 (0.32)	236.17 (43.68)	44.73 **a** (6.09)
	Tannin/Hexamine + PMDI + BA 2%	2.11 (0.26)	186.42 (21.24)	38.97 **ab** (3.05)
	Tannin/Hexamine + PMDI + BA 3%	2.01 (0.14)	185.88 (7.40)	36.75 **ab** (5.27)
	Tannin/Hexamine + PMDI + BA 4%	2.13 (0.58)	190.85 (25.13)	31.94 **b** (5.63)
Tannin 50 %	Tannin/Hexamine	2.15 (0.49)	214.94 (41.32)	45.13 **a** (0.65)
	Tannin/Hexamine + PMDI	2.14 (0.15)	177.34 (16.75)	41.71 **a** (2.14)
	Tannin/Hexamine + PMDI + BA 2%	2.31 (0.14)	193.47 (21.63)	36.59 **a** (9.70)
	Tannin/Hexamine + PMDI + BA 3%	1.61 (0.07)	198.41 (26.49)	37.06 **a** (5.53)
	Tannin/Hexamine + PMDI + BA 4%	2.15 (0.08)	105.45 (30.14)	11.03 **b** (4.54)

Table D.3 Fungal test results of poplar plywoods with treated tannin glue after EN 84 leaching test

	Formulations	Weight loss after leaching (Std. dev.) %	Humidity Average at the end of the test (Std. dev.) %	Average weight loss (Std. dev.) %
Tannin 45 %	Tannin/Hexamine	2.66 (0.21)	257.87 (61.76)	47.52 (6.45)
	Tannin/Hexamine + PMDI	3.04 (0.73)	170.87 (76.91)	42.68 (6.80)
	Tannin/Hexamine + PMDI + BA 2%	3.21 (0.47)	238.42 (54.78)	44.19 (9.13)
	Tannin/Hexamine + PMDI + BA 3%	2.63 (0.56)	239.58 (32.70)	44.17 (2.79)
	Tannin/Hexamine + PMDI + BA 4%	3.25 (0.94)	229.11 (74.03)	43.75 (8.18)
Tannin 50 %	Tannin/Hexamine	2.74 (0.27)	174.03 (48.06)	36.06 (7.62)
	Tannin/Hexamine + PMDI	2.67 (0.60)	177.95 (68.51)	41.53 (7.01)
	Tannin/Hexamine + PMDI + BA 2%	2.84 (0.49)	258.15 (72.13)	45.99 (5.43)
	Tannin/Hexamine + PMDI + BA 3%	2.42 (0.14)	207.98 (17.20)	43.92 (5.06)
	Tannin/Hexamine + PMDI + BA 4%	2.98 (0.09)	209.67 (60.64)	44.10 (5.91)

Table D.4 Fungal test results of beech plywoods with treated tannin glue before leaching.

	Formulations	Total retention of boric acid kg/m^3	Humidity Average at the end of the test (Std. dev.) %	Average weight loss (Std. dev.) %
Tannin 45 %	Tannin/Hexamine	0	174.29 (11.23)	47.40 **a** (1.99)
	Tannin/Hexamine +5% Boric acid	1.005	73.95 (11.94)	17.99 **b** (5.09)
	Tannin/Hexamine + PMDI +5% BA	0.934	66.00 (2.64)	14.40 **b** (5.33)
	Tannin/Hexamine +10% BA	1.973	78.80 (10.12)	13.70 **b** (4.10)
	Tannin/Hexamine + PMDI +10% BA	1.837	66.28 (4.08)	13.54 **b** (4.22)
Tannin 50 %	Tannin/Hexamine	0	192.46 (20.20)	52.02 **a** (4.30)
	Tannin/Hexamine +5% Boric acid	1.097	70.90 (14.49)	12.93 **b** (4.37)
	Tannin/Hexamine + PMDI +5% BA	1.013	59.85 (5.53)	13.31 **b** (2.94)
	Tannin/Hexamine +10% BA	2.150	84.64 (6.26)	9.87 **b** (0.60)
	Tannin/Hexamine + PMDI +10% BA	1.989	73.69 (15.20)	12.68 **b** (4.82)

Table D.5 Fungal test results of beech plywoods with treated tannin glue after EN 1250-2

		Weight loss after leaching %	Humidity Average at the end of the test (Std. dev.) %	Average weight loss (Std. dev.) %
Tannin 45 %	Tannin/Hexamine	3.05 (0.07)	155.74 (39.72)	48.07 **a** (6.14)
	Tannin/Hexamine +5% Boric acid	3.36 (0.22)	69.38 (17.88)	24.65 **b** (4.93)
	Tannin/Hexamine + PMDI +5% BA	3.31 (0.22)	84.67 (21.66)	19.07 **b** (9.44)
	Tannin/Hexamine +10% BA	4.93 (0.40)	80.79 (11.10)	23.82 **b** (3.71)
	Tannin/Hexamine + PMDI +10% BA	4.98 (0.49)	90.88 (4.61)	20.91 **b** (0.13)
Tannin 50 %	Tannin/Hexamine	2.91 (0.20)	185.60 (18.85)	51.25 **a** (2.12)
	Tannin/Hexamine +5% Boric acid	2.76 (0.12)	94.91 (13.35)	18.83 **bc** (2.48)
	Tannin/Hexamine + PMDI +5% BA	2.90 (0.18)	78.12 (16.54)	15.98 **c** (4.99)
	Tannin/Hexamine +10% BA	3.44 (0.34)	73.58 (10.48)	24.90 **b** (8.32)
	Tannin/Hexamine + PMDI +10% BA	5.23 (2.72)	90.96 (1.35)	19.02 **bc** (5.22)

Table D.6 Fungal test results of beech plywoods with treated tannin glue after EN 84

	Formulations	Weight loss after leaching %	Humidity at the end of the test (Std. dev.) %	Average weight loss (Std. dev.) %
Tannin 45 %	Tannin/Hexamine	3.21 (0.07)	163.15 (43.28)	48.44 **a** (5.59)
	Tannin/Hexamine +5% Boric acid	3.77 (0.09)	154.76 (48.68)	46.60 **a** (6.69)
	Tannin/Hexamine + PMDI +5% BA	3.90 (0.09)	159.70 (12.50)	48.32 **a** (4.04)
	Tannin/Hexamine +10% BA	5.22 (0.15)	93.90 (13.12)	29.21 **b** (2.28)
	Tannin/Hexamine + PMDI +10% BA	4.92 (0.75)	105.65 (12.88)	27.72 **b** (0.75)
Tannin 50 %	Tannin/Hexamine	3.19 (0.23)	128.68 (29.19)	43.44 **a** (2.82)
	Tannin/Hexamine +5% Boric acid	3.48 (0.12)	141.36 (63.97)	38.63 **a** (8.26)
	Tannin/Hexamine + PMDI +5% BA	3.65 (0.33)	132.60 (7.31)	40.13 **a** (2.95)
	Tannin/Hexamine +10% BA	5.13 (0.72)	107.76 (22.76)	28.71 **b** (4.66)
	Tannin/Hexamine + PMDI +10% BA	4.92 (0.61)	105.26 (19.08)	27.56 **b** (7.60)

Table D.7 Fungal test results of beech plywoods made of treated veneers before leaching

Tannin solution %	BA %	Core layer + treated -untreated	Retentions of Boric acid kg/m^3	Moisture content at the end of the test (Std. dev.) %	Weight loss (Std. dev.) %
Virulence controls of beech woods			0	43.90 (8.66)	23.98 (4.14)
Size controls of beech wood			0	136.48 (58.58)	47.12 **a** (9.64)
Control plywood			0	87.69 (18.00)	42.33 **a** (5.48)
Treated with water			0	62.55 (25.06)	35.99 **a** (4.62)
−	0.49	+	3.17	36.63 (0.75)	0.80 **c** (0.71)
−	0.49	−	2.11	35.48 (5.60)	0.85 **c** (0.77)
8.9	0.49	+	2.78	45.35 (5.19)	1.64 **c** (0.92)
8.9	0.49	−	1.85	54.06 (4.43)	5.26 **b** (2.54)
−	0.98	+	6.02	36.22 (1.56)	0.65 **c** (0.57)
−	0.98	−	4.01	39.39 (0.79)	0.76 **c** (0.66)
18.9	0.98	+	5.63	56.06 (7.53)	0.88 **c** (0.50)
18.9	0.98	−	3.57	50.29 (8.09)	1.07 **c** (0.11)

Table D.8 Fungal test results of beech plywoods made of treated veneers after EN 1250-2

Tannin solution %	BA %	Core layer + treated -untreated	Retentions of Boric acid kg/m^3	Moisture content at the end of the test (Std. dev.) %	Weight loss (Std. dev.) %
Control plywood			1.59 (0.79)	123.14 (32.90)	41.37 **a** (3.49)
Treated with water			1.54 (0.49)	117.76 (24.52)	38.96 **a** (2.38)
−	0.49	+	2.46 (0.37)	88.22 (5.17)	26.21**b** (1.84)
−	0.49	−	2.36 (0.39)	129.74 (4.06)	38.95 **a** (27.58)
8.9	0.49	+	2.74 (0.33)	71.74 (6.68)	11.82 **c** (1.95)
8.9	0.49	−	2.04 (0.31)	106.62 (8.53)	24.92 **b** (2.16)
−	0.98	+	3.42 (0.17)	77.93 (25.72)	23.32 **b** (2.70)
−	0.98	−	2.25 (0.14)	111.35 (14.97)	37.64 **a** (4.79)
18.9	0.98	+	2.31 (0.16)	54.52 (11.72)	5.59 **d** (2.74)
18.9	0.98	−	2.82 (0.14)	65.19 (2.23)	15.33 **c** (4.54)

Table D.9 Fungal test results of beech plywoods made of treated veneers after EN 84

Tannin solution %	BA %	Core layer + treated -untreated	Retentions of Boric acid kg/m^3	Moisture content at the end of the test (Std. dev.) %	Weight loss (Std. dev.) %
Control plywood			2.26 (0.17)	137.16 (16.90)	41.19 **ab** (6.06)
−	0.49	+	1.52 (0.09)	161.69 (27.79)	48.99 **a** (6.65)
−	0.49	−	2.37 (0.05)	151.43 (27.10)	45.73 **ab** (5.06)
8.9	0.49	+	1.90 (0.54)	91.84 (12.35)	33.75 **c** (2.82)
8.9	0.49	−	1.37 (0.39)	125.66 (8.48)	42.64 **ab** (0.53)
−	0.98	+	2.34 (0.10)	152.67 (1.45)	47.13 **ab** (1.33)
−	0.98	−	1.60 (0.20)	151.93 (15.92)	44.93 **ab** (2.88)
18.9	0.98	+	2.22 (0.31)	82.05 (14.83)	18.76 **d** (0.11)
18.9	0.98	−	2.89 (1.39)	66.85 (27.77)	29.58 **c** (4.07)

Table D.10 Fungal test results of beech plywoods made of treated veneers before leaching

Tannin solution %	BA %	Core layer + treated -untreated	Retentions of Boric acid kg/m^3	Moisture content at the end of the test (Std. dev.) %	Weight loss (Std. dev.) %
Not leached					
Control plywood			0	180.59 (33.48)	40.44 **a** (4.91)
Treated with water			0	169.43 (30.90)	39.78 **a** (0.97)
−	0.98	+	5.46	48.42 (10.62)	0.36 **b** (0.40)
8.9	0.98	+	4.00	67.47 (14.20)	0.51 **b** (0.43)
8.9	0.98	−	2.66	51.77 (10.92)	0.75 **b** (0.67)
Leached by EN 1250-2					
Control plywood				235.84 (27.40)	49.20 **a** (3.45)
Treated with water				256.54 (43.29)	54.82 **a** (2.61)
−	0.98	+	Unknown	241.73 (46.61)	44.66 **a** (6.01)
8.9	0.98	+	Unknown	73.34 (0.76)	4.51 **c** (10.24)
8.9	0.98	−	Unknown	132.48 (2.16)	25.13 **b** (2.12)
Leached by EN 84					
Control plywood				205.00 (54.03)	46.05 (2.85)
−	0.98	+	Unknown	206.56 (27.75)	44.51 (5.42)
8.9	0.98	+	Unknown	165.81 (26.37)	41.65 (2.66)
8.9	0.98	−	Unknown	158.10 (27.54)	43.81 (6.61)